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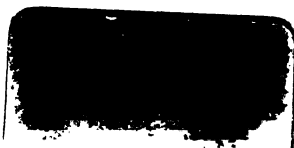
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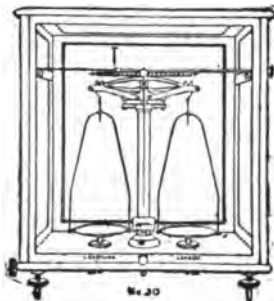
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No. 2275.—JULY 3, 1903.

SOME PRELIMINARY OBSERVATIONS ON THE ASSIMILATION OF CARBON MONOXIDE BY GREEN PLANTS.*

By W. B. BOTTOMLEY,
Professor of Botany, King's College, London,
and
HERBERT JACKSON,
Assistant Professor of Chemistry, King's College, London.

DURING an investigation by one of us some years ago on "Carbon Monoxide in some of its Physiological Effects," a few experiments were made on plants, and it was noticed that a hyacinth, which had commenced growth and was showing a few small leaves, continued to grow for some weeks when placed in a bell-jar in which the air had been replaced by a mixture of 80 per cent of carbon monoxide and 20 per cent of oxygen. As this was contrary to the usually accepted ideas as to growth of green plants in carbon monoxide, a number of experiments were recently commenced with a view to determining how far carbon monoxide could replace carbon dioxide as a source of carbon supply for green plants. Although the hyacinth grew in carbon monoxide the experiment was not considered conclusive, because of the large stores of carbohydrates in the bulb. Young plants of *Tropaeolum majus*, grown in sterilised sand and supplied with a nutritive solution free from all traces of carbonates, were therefore used. It was found that *Tropaeolum* plants would not grow in air in which the carbon dioxide had been replaced by an equal quantity of carbon monoxide. When, however, the relative solubilities of the two oxides of carbon in water were taken into account, and the amount of carbon monoxide was increased proportionately—about twenty times as much carbon monoxide as carbon dioxide—the plants grew well, being healthy and normal. Experiments were also made with varying proportions of carbon monoxide in air free from all traces of carbon dioxide. The plants grew freely and well in proportions varying from 1 to 70 per cent of carbon monoxide, when care was taken that as the higher percentages of carbon monoxide were reached, oxygen was added so as to keep the amount of this gas approximately equal to that in normal air.

One very significant fact was noticed during the experiments. When in bright sunshine a negative pressure was always observed in the bell-jars containing plants growing in carbon monoxide. This result tends to confirm Baeyer's theory of photosynthesis. In normal photosynthesis the volume of oxygen given off is equal to the volume of carbon dioxide undergoing decomposition. If, however, carbon monoxide be used directly by the plant, only half the

amount of oxygen would be given off, hence the negative pressure.

Experiments were also made to find if starch was formed in plants growing in carbon monoxide. *Tropaeolum* plants growing in water culture solutions were placed in the dark for forty-eight hours, when the leaves were shown by the iodine test to be free from starch. Some of the plants were then placed in air free from carbon dioxide; others in carbon dioxide free air, but containing 10 per cent of carbon monoxide. All were then exposed to sunlight for three days, and again examined for starch. The plants grown in carbon dioxide free air had formed no starch, whilst those grown in carbon monoxide gave the iodine test most markedly. Sections of the green stems showed quantities of starch grains in the ground tissue, especially crowded around the vascular bundles, in the plants grown in carbon monoxide, but none in those grown in carbon free air.

Experiments on the germination and growth of seeds in carbon monoxide also gave satisfactory results. Seeds of *Lepidium sativum* were planted in sterilised sand, and placed in a mixture of 65 per cent carbon monoxide and 35 per cent oxygen. The seeds germinated, and formed healthy plants, growing quite normally for three weeks. Certain preliminary determinations of the amount of carbon in the seeds and in the plants point to the accumulation of organic carbon, and as the only possible source for this increase of carbon is the carbon monoxide, some of it must have been assimilated. These results are so important and the results so striking that it has been thought advisable to repeat the determinations with new and specially devised apparatus before quoting figures. Also it is intended to carry out further experiments with carbon monoxide, and with compounds in which the CO-group exists in combination.

In all these experiments with carbon monoxide, great care was taken that efficient absorbers of carbon dioxide were used, and the pressure in the bell-jars was regulated by potash-sealed valves.

The present communication is only a note to indicate the general bearings of the research, and does not give any account of many experiments and observations of interest which the authors hope to give later in a detailed paper.

Decarburation of Steels and Thin Metallic Plates by Evaporation in vacuo.—G. Belloc.—In a previous research the author discovered that steel, when heated to about 1000° in a vacuum obtained either from air or hydrogen, is decarburised. His further experiments prove that the decarburation is due to the presence of gases occluded in the metal.—*Comptes Rendus*, cxxxvi., No. 22

* A Paper read before the Royal Society, June 18, 1903.

By C. T. HEYCOCK and F. H. NEVILLE.

* Abstract of the Bakerian Lecture of the Royal Society, delivered February 26, 1903.

of all that such curves tell us with certainty. They do not tell us whether the solids forming are the pure metals, or pure compounds, or crystalline solid solutions of the metals. Other experiments are needed to decide such questions.

The other great branch of the study of alloys consists in the microscopic examination of the solid alloys after they have cooled to ordinary temperature; that is to say, after they have, in general ceased to undergo change. Between these two series of experiments there is an enormous gap of temperature, it may be 1000 or 500 degrees, and it is in this range of temperature that the whole life history of the alloy, regarded as an organism, is to be found. The only fruitful experiments we know of dealing with this intermediate region are the cooling curves of Roberts-Austen and Stansfield. These observers traced automatically the whole of the cooling of the bronzes, and obtained some remarkable results. They found that the evolution of heat at the freezing-point was often succeeded at much lower temperatures by other evolutions of heat, and that many of these must have occurred after the alloy had wholly solidified. These thermal changes point to important chemical or physical changes, though they do not tell us what these changes are. They suggest, however, that the final patterns found by the microscope in the solid alloys are likely to be very complicated, as they may contain several records superposed the one on the other. We found these patterns very beautiful, but hopelessly complicated.

It occurred to us, and this is the method of the paper, that we could simplify the phenomena by a systematic chilling of the ingots at selected temperatures. A number of small ingots of the same alloy were placed in separate tubes in a bath of tin, together with a recording pyrometer, the temperature was raised above the freezing-point of the alloy, and the whole very slowly cooled, the slow cooling being an essential feature of the experiment. Ingots were then extracted at selected temperatures, and rapidly chilled by immersion in water. The microscopic examination of these chilled ingots showed that it was quite easy to distinguish the large crystals, that had formed during the slow cooling preceding the chill, from the matter that was liquid when the ingot was withdrawn from the furnace.

Successive chills of an alloy exhibit the solid growing in amount as the temperature falls, and finally show the ingot completely full of solid. We thus obtain, with very reasonable accuracy, the temperature of complete solidification of the alloy; and by applying the method to alloys with different percentages of tin we have traced a new curve, the "solidus," or curve of complete solidification. The solidus of the bronzes is the second line of the

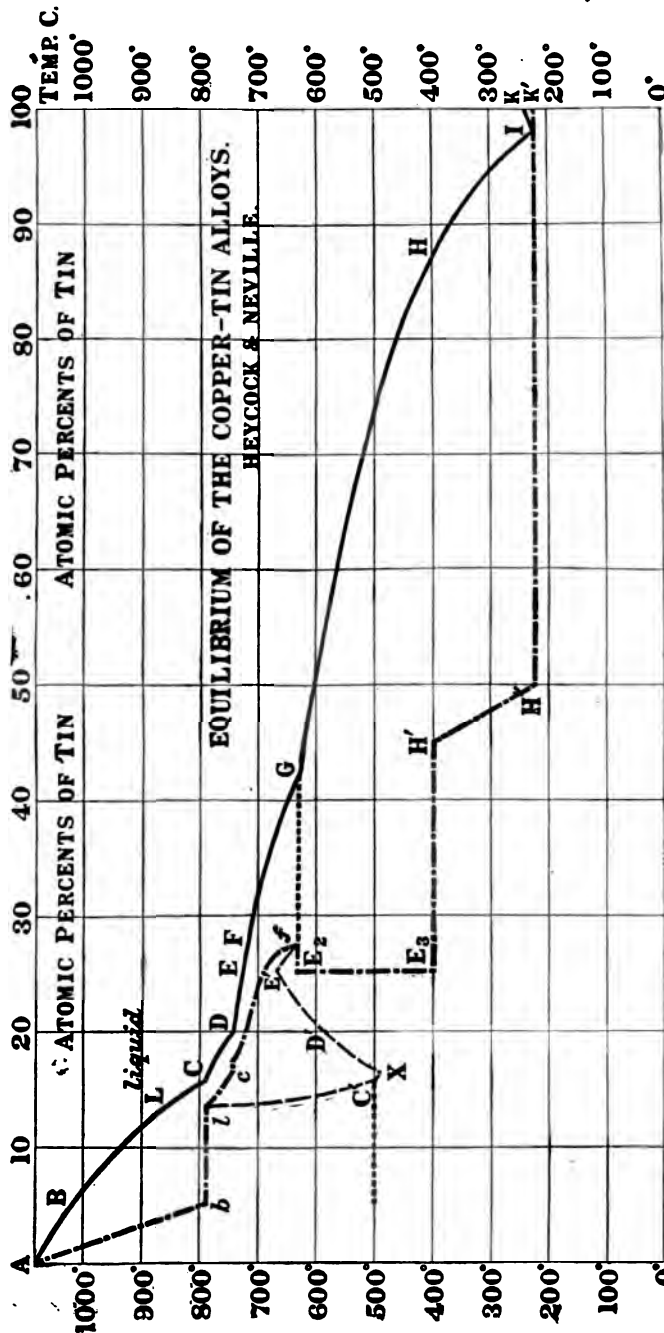


diagram. It is a remarkable line, made up of sloping, horizontal and vertical branches. As in the freezing-point curve, each branch corresponds to the crystallisation of a different solid.

In the notation of Prof. Roozeboom, the upper curve ABC . . . I, is called the liquidus, because all wholly liquid alloys lie above it; and the solidus, *AbcdefE₂E₃H'H''I*, is so named because all wholly solid alloys lie below it.

The solidus of the bronzes is remarkable for the very narrow range of temperature within which some alloys pass from the wholly liquid to the wholly solid state.

According to Roozeboom's theory, each sloping branch of the solidus, and there are four such in the diagram, corresponds to the crystallisation out of the liquid of a different series of solid solutions, each vertical part to the crystallisation of a pure body, and each horizontal part to the case of the solid alloy at temperatures immediately below the solidus, being a complex of two substances. Our examination of the chilled ingots has completely verified all these statements.

The evolutions of heat observed by Roberts-Austen and Stansfield at temperatures corresponding to the point C, D, G, and H are due to definite chemical transformations in which one solid is decomposed and another is formed. Chills taken immediately above and below these critical temperatures reveal the nature of each change most clearly.

The transformations at C, D, and especially at H, are very slow, and do not become complete unless the temperature is maintained constant for hours or days at a point slightly below the transformation temperature, but all these temperatures can be made to agree exactly with theory if time is allowed for them. The change at the G temperature is the breaking up of a solid solution into a mixture of the compound Cu₃Sn and liquid, and is instantaneous; here we have a case of a solid partially melting as it cools.

The curve *ixE'f* forms with the part of the solidus immediately above it an area, roughly triangular, within which all the alloys appear to be uniform solid solutions, but, as soon as an alloy cools to the curve, it becomes saturated, and a new body crystallises out of the solid solution. One branch of the curve *ixE'f* corresponds to the crystallisation of a body rich in copper, the other to the crystallisation of a body rich in tin which is probably the pure compound Cu₄Sn. The angle X (or rather C) is the eutectic angle at which both bodies crystallise together, the whole phenomenon being exactly like crystallisation out of a liquid.

All the results obtained from the study of the chilled alloys are in harmony with the pyrometric work of Roberts-Austen and Stansfield, and many of the changes we have examined correspond to an evolution of heat recorded by them.

The paper is an extension of a short paper published by us in the *Proceedings of the Royal Society*, Dec., 1901.

The Electrolysis of Aqueous Solutions with Platinised Electrodes, and the Electrolytic Formation of Dithionates.—F. Foerster and F. Friessner.—When we electrolyse solutions of sulphuric acid or soda, by means of electrodes covered with platinum black, we observe that the electromotive force of polarisation increases slowly until it reaches 2 volts, or 1·1 volt more than that of a similar voltmeter, of which the electrodes have been saturated recently with hydrogen and oxygen gas at the atmospheric pressure. Quantities of oxygen, very small, however, thus brought to the anode, appear to exist there in the dissolved state, and can be utilised for the purpose of effecting certain oxidations. Thus, a solution of neutral sulphite of sodium which, being a bad conductor, does not require the use of a porous diaphragm, is able to give dithionate up to 53 per cent of the original salt if we operate below 1·85 volts with freshly platinised electrodes, and the anode having been previously saturated with oxygen by electrolysis for forty hours, from NaHO with a current of 0·25 ampère.—*Berichte*, vol. xxxv., p. 2515,

A NEW METHOD FOR THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF OSMIDES OF IRIDIUM.

By MM. LEIDIÉ and QUENNESSEN.

DURING the examination of the process used by MM. Sainte-Claire Deville and Debray for the analysis of osmides of iridium, we have made a certain number of observations. Thus, when the product of the attack of the osmides by binoxide of barium is treated with dilute acids there is a disengagement of peroxide of ruthenium, which is volatilised at the same time as the peroxide of osmium. Again, in the separation of the iridium and ruthenium, the precipitation of Ru₂Cl₆ by chloride of ammonium cannot be complete, and when we have treated the metals which result from the calcination of the insoluble double chlorides with fused potash and nitrate of potassium, a portion of the iridium may dissolve in water with the ruthenium, so that the binoxide of ruthenium precipitated by acids may carry binoxide of iridium with it. Finally, they estimate the osmium by difference, by driving it off in the form of peroxide, so that they have nothing to check the weight of this element but the estimation of the numerous impurities contained in the osmides.

The method we are about to give is an application of our previous researches. It is based on the action that fused binoxide of sodium has on the metals of the platinum group (*Bull. Soc. Chim.*, [3], vol. xxvii., p. 179), and on the analytical properties of the double nitrites of these metals (*Comptes Rendus*, vol. cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9).

I. The Attack of Osmide of Iridium.

As it is exceptional, even in the residues from the attack of platinum ores, to find osmides in a sufficiently finely divided state to be attacked directly, and as the osmides, in their usual condition, resist all reagents and cannot be pulverised, it is necessary first to decompose them. For this purpose we use the old method employed by Sainte-Claire Deville and Debray, eliminating the zinc from the alloy by heat, as they did, its elimination by means of hydrochloric or sulphuric acids is not to be recommended; the former dissolves the platinum metals, the latter leaves an alloy of zinc which may deflagrate in the presence of binoxide of sodium.

Thus we melt, in a nickel crucible, 10 grms. of hydrate of sodium (previously fused), and into this we gradually throw an intimate mixture of 10 grms. of osmide of iridium and 40 grms. of binoxide of sodium; this must be stirred continuously with a nickel spatula, and heated sufficiently to keep the mixture in a semi-fluid condition. The operation should not last more than about half-an-hour. The addition of soda has for its object the lowering of the fusing-point of the binoxide, and of diminishing considerably the attack on the crucible. The material is run out on a sheet of nickel. When cold it is broken up, and thrown in small portions at a time into a porcelain crucible covered with a funnel, and containing a litre of water; the portion adhering to the crucible is also treated with water. All the liquors are added together, and when cool they are left to stand in decantation flasks with ground stoppers. The clear liquor is decanted, and the insoluble residue taken up with hypochlorite of soda diluted with its own volume of water to dissolve the binoxide of ruthenium which might be formed by decomposition brought about by the water. The wash waters are added to the original solution.

The solution thus obtained contains all the osmium and ruthenium in the form of osmiate and rutheniate, with the greater portion of the iridium in the form of iridiate. It may contain also traces of gold and palladium, as well as chromium, aluminium, and manganese from the ore, in the form of alkaline salts. The insoluble portion contains the remainder of the iridium, the iron from the ore, and the nickel from the crucible, with sometimes traces of platinum and rhodium.

II. Separation of Osmium and Ruthenium.

The solution is placed in a glass retort of which the drawn out neck is fitted into the neck of a flask having a lateral tube, the central tube forming a hydraulic joint; such a flask is similar to the one used for the condensation of peroxide of ruthenium (Joly, "Encyclopædie Chimique de Frémy," vol. iii., No. 3, p. 236). This flask is followed by two similar ones forming the condensing apparatus. They are all three plunged into iced water, and two-thirds filled with hydrochloric acid diluted with two volumes of water: by grinding all the joints with emery, all loss of condensable vapours is prevented. The two first flasks will probably be sufficient, the third acts as a control. A current of chlorine is passed through the retort, cold at first, then when the liquid commences to give off bubbles of oxygen, it is heated to about 70°. The osmium and ruthenium are transformed into volatile peroxides, OsO_4 and RuO_4 , which condense in the flasks, the iridium into sesquichloride, which remains in the retort in solution, thanks to the excess of soda. The contents of the retort should remain alkaline until the end of the distillation, first on account of the action of hydrochloric acid on RuO_4 , and afterwards because the chlorine passing through the cold recipients, gives hydrate of chlorine which obstructs the tubes. (It is this hydrate that Joly must have mistaken for an emulsion of RuO_4 .) If by chance the contents of the retort become acid, soda must be added. The end of the operation can be determined by making sure that the drops, which distil over, do not blacken a solution of sulphuretted hydrogen.

Under the influence of hydrochloric acid, the peroxide, RuO_4 , is transformed into the sesquichloride, Ru_2Cl_6 , which is stable; while the peroxide, OsO_4 , does not undergo any change. This reaction, commencing in the cold, ought to be completed by the action of heat. For this purpose the contents of the three flasks are placed together in a retort, connected with a system of three condensers similar to those in the preceding apparatus. The flasks are plunged into ice, they are filled up to two-thirds, the first with hydrochloric acid diluted with two volumes of water to arrest the incompletely transformed peroxide, RuO_4 ; the two others are filled with a solution of soda at 12 per cent of NaOH , treated with 2 per cent of alcohol, to transform the peroxide, OsO_4 , into osmiate of sodium. The contents of the flask are heated to about 70°, while passing a slow current of air. When no more peroxide of ruthenium distils over (the drops distilled should not colour hydrochloric acid brown), the contents of the first condensing flask are returned to the retort, and the flask is filled up to two-thirds with an alkaline alcoholic solution like that in the next two flasks. The distillation is then pushed to its completion; that is to say, until the drops no longer blacken sulphuretted hydrogen; as a rule, to obtain this result, it is necessary to distil half the contents of the retort. The osmium is then contained entirely in the condensing flasks, in the form of osmiate, and the ruthenium is in the retort in the form of sesquichloride; these two compounds not being volatile are easily determined in subsequent operations.

To make certain that the separation of the Os and Ru is complete we proceed in the following manner:—A solution containing OsO_4 and RuO_4 becomes brown under the influence of hydrochloric acid, owing to the formation of brown Ru_2Cl_6 . A solution containing Ru_2Cl_6 and OsO_4 , treated with carbonate of baryta, freshly prepared and free from baryta, gives a precipitate of Ru_2O_3 ; the solution, freed from the chloride of barium formed by means of SO_4Na_2 , should not become violet in the presence of an alcoholic solution of soda (formation of violet osmiate).*

* We propose to substitute this method for the separation of osmium and ruthenium for that of MM. Sainte-Claire Deville and Debray, adopted at first by M. Liedié, and which figures as his general method for the extraction and separation of the metals of the platinum group. (See above).

III. Separation of Iridium.

The contents of the retort from which the osmium and ruthenium have been driven in the first distillation, are acidulated with hydrochloric acid. The residue, insoluble in water, resulting from the attack of the osmide by Na_2O_2 , is dissolved in hot dilute hydrochloric acid; this residue is easily soluble, while the other methods of attack (potash and nitrate of potash, for example) give a mass which is very difficult to dissolve, even with aqua regia. If any crystals of unattacked osmide are found, owing to their being insufficiently finely divided, they must be collected and subtracted from the original weight. The two solutions are united; the solution then contains all the iridium, as well as the iron in the ore, and the nickel from the crucible; it may contain traces of gold also, as well as rhodium and platinum, and any other foreign metal associated with the osmide, such as chromium, aluminium, silicon, manganese, copper, &c. The solution is heated, and to precipitate all the foreign metals, it is treated successively with nitrite of sodium and carbonate of sodium, following the instructions given by one of us *à propos* of the general method for the separation of the metals of the platinum group (Liedié, *Comptes Rendus*, vol. cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9). Nothing remains in solution but the double nitrite of iridium and sodium; this is transformed into chloroiridate by warm hydrochloric acid. Then, as the large amount of chloride of sodium present in the solution might be prejudicial, either to the precipitation of the chloroiridate by chloride of ammonium, or to the precipitation of the iridium by magnesium, the cooled solution must be saturated with hydrochloric acid gas. The precipitated chloride of sodium is drained and washed with hydrochloric acid; the solutions, which only contain chloroiridate of sodium with a little chloride of sodium, are added together.

IV. Estimation of the Metals.

Osmium.—The contents of the flasks containing the osmiate of sodium are added together (if they are not decidedly violet they must be heated gently), and strips of aluminium are plunged in; the osmium is deposited in the metallic form, while the aluminium dissolves in the soda. Care must be taken not to add too much aluminium at first, as the alumina formed, not finding a sufficient quantity of soda to enable it to go into solution, would precipitate an aluminate which is very difficultly soluble both in acids and in alkalis. When the solution is once decolorised, the precipitated osmium, which is very dense, is washed by decantation, first with water to remove the aluminate of soda, and then with 5 per cent sulphuric acid to remove the remaining excess of aluminium, along with the iron accompanying this metal.

This osmium is thrown on an asbestos filter connected with a filter-pump and well-washed; the filter must have been treated first with 20 per cent sulphuric acid, then washed, dried, calcined at a red heat, and weighed in a closed tube. The osmium is dried in a bell-glass filled with hydrogen, then heated to dull redness, and cooled in a current of this gas; the hydrogen is only driven off by the carbonic acid when the whole has been cooled, as the latter gas oxidises the osmium when hot. The filter is weighed again in a closed tube.

As a check, the osmium may be driven off in the form of the peroxide, OsO_4 , by heating the filter to redness in a current of oxygen, and then weighing it again.

Ruthenium.—The hydrochloric solution containing the sesquichloride, Ru_2Cl_6 , is evaporated gently to a syrupy consistence, so as to drive off the excess of acid. The residue is taken up with 50 or 60 c.c. of water, and a few fragments of magnesium added gradually; the solution becomes clear and takes a blue tint; this reaction is characteristic of ruthenium, and was wrongly attributed to osmium by Fischer, the latter being completely decolorised. The solution is then decanted, and the powder is washed with 5 per cent sulphuric acid, so as to remove the excess of magnesium. Throw on a filter, wash with water, dry,

and after incinerating the filter at the lowest possible temperature, heat the whole in hydrogen to a red heat, then allow to cool in carbonic acid, and weigh.

Iridium.—The solution containing the chloroiridate of sodium is evaporated to drive off the large excess of hydrochloric acid present. The residue is taken up with water, and diluted to a volume of 500 c.c. From this we take 50 or 100 c.c., according to the probable proportion of iridium present, and add gradually some fragments of magnesium until it is completely decolorised. The powder is washed with 5 per cent sulphuric acid, then with water, and dried; after the incineration of the filter, it is heated to redness in hydrogen, cooled in a current of carbonic acid, and weighed.

In all these operations we use sulphuric acid rather than hydrochloric acid, which would dissolve a portion of the precious metal.

V.

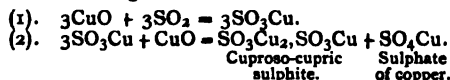
Analyses conducted in this manner have been carried out on osmides from various sources. M. Riche, Directeur des Essais, at the Hôtel des Monnaies, has been good enough to supply us with osmides resulting from the operations to which gold is subjected during purification. In these osmides we have never met with any but the four following metals:—Iridium, osmium, ruthenium, and iron. On the other hand, in osmides from the residues from the treatment of the metals of the platinum group, we find traces of these latter metals, as well as the commoner ones accompanying the ore; the separation of the precious metals is made then by the general method which has been given already by one of us (Leidié, see above).

It would seem thus to be well established, as MM. Sainte-Claire Deville and Debray were inclined to believe, that when osmide of iridium is perfectly freed from the metals of the platinum group with which it is often mixed; it does not contain any other metals than the four we have just mentioned above.

A METHOD OF EXTRACTING COPPER FROM ITS SULPHIDE ORES.*

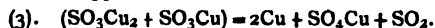
By GUSTAVE GIN.

Dissolved sulphurous acid possesses the known property of attacking oxide and carbonate of copper, forming an unstable sulphite of the binoxide, which is gradually transformed into a mixture of cuproso-cupric sulphite and sulphate, according to the reaction—



Cuproso-cupric sulphite is slightly soluble in water, but easily soluble in solutions of sulphurous acid or cupric sulphate.

On heating the solution to 180° (under a pressure of 10 kilograms.) it loses sulphurous acid, while cupric sulphate and metallic copper are formed:—



If we group the formulæ 1, 2, and 3 together we see that, taken altogether, the reactions correspond to $4\text{CuO} + 2\text{SO}_2 = 2\text{Cu} + 2\text{SO}_4\text{Cu}$; that is to say, that half the copper can be obtained in the metallic state, and the other half in the form of sulphate.

On the above principles I have devised a process for the treatment of copper ores, utilising the sulphurous acid produced by roasting them in such a manner that the active reagents may be extracted entirely from the ore itself and from the atmosphere.

The ore is roasted in such a manner that the whole of

the sulphide of copper is transformed into binoxide or sulphate, and the whole of the iron into peroxide.

Then it is lixiviated methodically by means of a solution of sulphurous acid prepared in the ordinary manner. A saturated solution of cuproso-cupric sulphite and sulphate of copper is obtained, containing at the same time a certain proportion of sulphite and sulphate of protoxide of iron. The sulphite of the sesquioxide of iron in the presence of an excess of sulphurous acid is transformed according to the reaction, $\text{SO}_2, \text{Fe}_2\text{O}_3 + \text{SO}_2 = \text{SO}_4\text{Fe} + \text{SO}_3\text{Fe}$.

The saturated solution of the salts of copper and iron is pumped into a copper boiler, where it is heated up to 180°, by which it is expected a pressure of 10 kilos. is produced. At this temperature the sulphite and the ferrous sulphate are completely insoluble, and are precipitated. As for the cuproso-cupric sulphite, it is dissociated and loses two-thirds of its copper in the metallic state, and at the same time sulphate of copper is formed.

The cloudy liquid is forced by its own pressure through a filter-press heated by steam circulating round the plates, an apparatus I patented some time ago for the mechanical separation of cupric and ferrous sulphates, but which could be replaced by any other arrangement for the filtration of solutions at a high temperature.

In this manner we obtain a solution of sulphate of copper which can be cemented or treated for crystallised sulphate, and a precipitate containing metallic copper, and sulphite and sulphate of the protoxide. This precipitate is washed with pure water, which becomes saturated with sulphate of protoxide of iron, which may be extracted by crystallisation.

The residual sulphite is then oxidised by moist air, and gives sulphate of the protoxide, which can be eliminated by a fresh washing, and there remains finally metallic copper of great purity, which is melted and run into ingots.

INFLUENCE OF THE NATURE OF THE CATHODE ON THE QUANTITATIVE SEPARATION OF METALS BY ELECTROLYSIS.

By A. HOLLARD.

In electrolytic analysis the metals are divided into two principal classes, according to whether they are or are not capable of being deposited on the cathode from a strongly acid solution. The metals which will not deposit in strongly acid solutions are those which require, for covering the cathode, electric tensions higher than the tension at which hydrogen commences to be given off. We see thus that, under the influence of these high tensions, a strongly acid solution (that is to say, a solution in which the pro-

portion of H ions is very high) gives rise to a disengagement of hydrogen at the cathode so abundant that all metallic precipitation becomes impossible thereon.

The metals which are capable, on the other hand, of depositing on the cathode in strongly acid solutions are those which require for this precipitation, tensions lower than the tension of polarisation of hydrogen; their deposition therefore is not interfered with by the hydrogen.

If we call the tension of polarisation of hydrogen zero, we shall have the following values for the tension of polarisation of the principal metals (Nernst and Wilmore, *Zeit. f. Elektrochemie*, November 8, 1900).

As can be seen, the classification of the metals into two groups, has for its basis the position occupied by hydrogen in the table of the tension of polarisation of the metals. But this position is only fixed in practice in electrolytic analysis if we always use platinum cathodes. As a matter of fact, hydrogen—as has been shown by Caspari (*Zeit. für Physik. Chem.*, 1899, vol. xxx., p. 89)—has a tension of polarisation which is variable with the metal constituting the cathode. If, therefore, we use, as we have done, cathodes formed of other metals than platinum,

* A Paper read at the Fifth International Congress of Chemistry at Berlin. Section III.

the tension of polarisation of hydrogen takes another position in the accompanying table; this causes a certain number of metals to pass from one group to the other.

TABLE I.

Metals not Deposited in Strongly Acid Solutions.

Zn	..	..	..	..	..	+0.77
Cd..	..	..	..	..	..	+0.42
Fe..	..	..	..	..	..	+0.34
Co	}	..	..	..	..	+0.23
Ni		..	..	..	..	+0.19
Sn..	..	..	..	..	..	+0.19
Pb..	..	..	..	..	..	+0.15
H ..	..	..	..	..	..	0.00

Metals Deposited in Strongly Acid Solutions.

As..	..	..	..	..	..	-0.29
Cu	..	..	..	..	..	-0.33
Bi..	..	..	..	..	..	-0.39
Sb..	..	..	..	..	..	-0.47
Hg	..	..	..	..	..	-0.75
Ag	..	..	..	..	..	-0.77
Pd..	..	..	..	..	..	-0.79
Pt..	..	..	..	..	..	-0.86
Au	..	..	..	..	..	-1.08

It is conceivable, therefore, that, by the choice of a suitable metal for the cathode, we may succeed in separating two metals of the same group, of which the tensions of polarisations are too near together to enable us to separate by means of a platinum cathode. For this purpose it suffices to choose a metal for the cathode which gives hydrogen a tension of polarisation between those of the two metals to be separated. The element whose tension of polarisation is the lowest will be precipitated then alone in a strongly acid solution.

For choosing the most suitable metal for the cathode, the following table must be consulted; it was drawn up by Caspari, and gives the different values of the tension of polarisation of the hydrogen set free on different metals used as the cathode in a solution of normal sulphuric acid.

TABLE II.

Pt, platinised	..	..	..	..	0.00
Au	..	..	..	..	0.02
Fe (in NaOH)	..	..	..	..	0.08
Pt, polished	..	..	..	..	0.09
Ag	..	..	..	..	0.15
Ni	..	..	..	..	0.21
Cu	..	..	..	..	0.23
Pd	..	..	..	..	0.46
Cd	..	..	..	..	0.48
Sn	..	..	..	..	0.53
Pb	..	..	..	..	0.64
Zn (in acid solution of zinc)	..	..	..	..	0.70
Hg	..	..	..	..	0.78
Cu (amalgamated)	..	..	..	..	0.51
Pb	..	..	..	..	0.54
Cd	..	..	..	..	0.68

But it is not sufficient, however, to choose for the cathode a metal that has the property of raising the tension of polarisation of hydrogen above that of the metal to be precipitated, for this property of the metal constituting the cathode disappears at the moment it is covered by the precipitated element, and then the cathode plays the same part as if it were made exclusively of the metal precipitated. It is therefore necessary, further, for the continuation of the precipitation, that the latter metal also should have the property of raising the tension of polarisation of hydrogen above its own tension of polarisation.

By using cathodes formed of the same metal that it is proposed to deposit, we see from the preceding table that we can precipitate from strongly acid solutions, not only the metals of which the tensions, in Table I., are lower

than that of hydrogen, but also lead, tin, and cadmium. In fact, the tension of polarisation of lead (+0.15) is decidedly lower than that of hydrogen liberated on a lead cathode (+0.64); the same holds good with tin and cadmium.

As an example of the application of this new method of analytical separation, we will describe the separation of zinc and cadmium—metals that we have been unable to separate when using a platinum cathode,* on account of the closeness of their tensions of polarisation. On the other hand, we have been able to effect their separation with either a cadmium or tin cathode in a very acid bath. Our cadmium and tin cathodes were nothing more than platinum-gauze electrodes, covered electrolytically with cadmium or tin.

The cadmium and the zinc, brought into solution in the state of sulphates, were treated with 10 grms. of sulphate of ammonia and an excess of 5 c.c. of concentrated sulphuric acid. The solution, diluted to 300 c.c., was electrolysed with a current of 0.3 ampère. The following results were obtained:—

Experimental Results.

Amount weighed.†		Cd deposited.
Cd.	Zn.	
Grm.	Grms.	Grms.

On a Cathode of Tinned Platinum-gauze.

0.1991	2	0.1972
0.2996	2	0.3010
0.1996	1	2.002

On a Cathode of Cadmium-plated Platinum-gauze.

0.1991	2	0.1984
0.2488	2	0.2484
0.1991	0	0.1968

On a Cathode of Platinum Gauze.

0.2000	2	0.0002
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—Bull. Soc. Chim., Series 3, vol. xxix., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 17th, 1903.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

Messrs. E. S. Beaven and C. Rawson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy W. Gent, 792½, Ridge Street, Newark, N.J., U.S.A.; Henry William Lawrence, Wellington, New Zealand; Herbert Stanley Redfern, B.Sc., Ningpo, China; Frank Gurney Smith, 7, Luxemburg Gardens, Brook Green, W.

PRESENTATION OF THE LONGSTAFF MEDAL.

The President spoke as follows:—We have so recently celebrated the Centenary of the Atomic Theory that it is a matter of interest to notice that, in the award of the Longstaff Medal on the present occasion, we honour the practical fulfilment of the deductions from that great conception. Dalton himself represented in his diagrams atoms of solid bodies like ice arranged with reference to the crystalline form of the solid, but for three-quarters of a century

* Both in slightly acetic solutions and in cyanide solutions and no matter how small the current used.

† The cadmium used in the first three experiments contained:—Pb=0.231 per cent, Fe=0.000 per cent, Zn=0.000 per cent. The cadmium used in the next three experiments contained:—Pb=0.245 per cent, Fe=0.193 per cent, Zn=0.000 per cent. This amount of impurity has been subtracted from the amounts actually weighed, and it is the differences thus obtained that figure in the column "Amount weighed."

successive writers could merely speculate as to their possible order in space of three dimensions. The discoveries of Pasteur in connection with hemihedrism in crystals, and the study of the lactic acids by Wislizenus, prepared the way for the development of the theory of stereo-chemistry by van't Hoff and le Bel in 1874. But while that theory has prospered and has led to innumerable developments in the study of the compounds of carbon, and although it must have been always obvious that if the idea of a tetrahedral configuration was valid for compounds of one element a corresponding idea should be equally applicable to those others, the demonstration of the facts upon which such a development must rest has only been accomplished within the last four years.

To Professor William Jackson Pope the Council has awarded the Longstaff Medal by a unanimous vote, for his researches on the stereo-chemistry of compounds of elements other than carbon. In 1893, Professors Kipping and Pope prepared the *d*-bromo- and *d*-chlorocamphorsulphonic acids, and by the use of these and other powerful optically-active acids, Mr. Pope has succeeded, not only in resolving into their active components certain racemic bases which had been found irresolvable by the use of tartaric acid, but in 1889, by the use of *d*-camphorsulphonic acid, he separated the dextro- and lævo-modifications of a synthetic tetraalkylammonium base, and thus definitely established the existence of asymmetric optically active nitrogen compounds.

Since that time, by similar methods, he has obtained the dextrorotatory methylethylthetine, a dextrorotatory tin compound, and both forms of a selenetine, thus demonstrating the fact that the elements nitrogen, sulphur, tin, and selenium are each capable, like carbon, of producing asymmetric combinations possessing optical activity. We therefore now possess direct experimental evidence in regard to the compounds of carbon, tin, sulphur, and selenium, as tetrad elements, and of nitrogen as a pentad, so that it may confidently be expected that not only will the phosphorus series of elements be found capable of producing pairs of enantiomorphous compounds, but, possibly, similar modifications of oxonium bases may be discovered, and some of the metals, such as platinum, cobalt, and chromium, may be found to exhibit similar phenomena. The doctrine of valency, no less than the doctrine of atoms, in its application to all ordinary terrestrial chemical phenomena, is thus triumphantly established.

Professor Pope, it gives me great pleasure to be the medium of communicating to you the congratulations of the Council, and in handing you the Longstaff Medal I express the feelings of the whole chemical world when I say that we trust you will have health, and strength, and time to continue the researches which have already yielded such a rich harvest of splendid results.

Professor POPE, in expressing his sense of the honour done him by the award of the Longstaff Medal, desired to acknowledge gratefully the assistance which the Research Fund Committee had given to his work; it would be difficult to over-estimate the extent to which the Research Fund of the Chemical Society has contributed to the encouragement of chemical investigation in Great Britain. He wished also to record his indebtedness to his old friend and teacher, Dr. H. E. Armstrong, who first taught him to look upon our science as a living and growing branch of knowledge, and inspired him with a desire to contribute something towards its development.

Dr. G. B. LONGSTAFF, in expressing his great pleasure at being present on this occasion, said that the researches for which Professor Pope had been awarded the medal considerably advanced our conceptions of the atomic theory in so far as they broke down some of the apparent barriers between carbon and the other elements. He recalled the fact that his father, who had been a friend of Dalton's, was not only a Fellow of this Society from its commencement, but also the founder of Chemical Societies in Edinburgh and Glasgow, and was, moreover, instrumental in placing

on a working basis the Research Fund (first suggested by Dr. Millar) to which Professor Pope had referred. Nevertheless, the name of the donor of the medal would have remained obscure except for the reflected light thrown on it, as it were, by the great names of an already long succession of eminent medallists.

A ballot for the election of Fellows was held and the following were subsequently declared duly elected:—Henry James Aubrey; George Barger, B.A., B.Sc.; Colin Noel Bennett; Wilfrid W. O. Beveridge; Charles Drake Bibby; Henry J. W. Brennand, B.A., M.B.; William Godsell Burghard; Ernest Bury, M.Sc.; Thomas Campbell; Albert James Carrier, B.Sc.; Edwin Jesse Fairhall; William Hunter Gandy; Francis Gerald Harmer; Frank William George King; Henry Wolff Levy; John Howard Lindsay; Charles Edwin L. Livesey, B.Sc.; John Christopher Mann; Alfred Ernest Moore, B.A., B.Sc.; Arthur Moore; George Marshall Norman, B.Sc.; George Harry Parry; Charles Stanley Purcell; Thomas Rhind, M.R.C.S.; Charles Joseph Smith; James Cruickshank Smith, B.Sc.; Dennis Tyrrell; Norbert Van Laer; Sydney H. Woolhouse, M.A., B.Sc.

Of the following papers those marked * were read:—

*96. "*The Estimation of Arsenic in Fuel.*" By T. E. THORPE.

An account was given of a method of estimating the amount of arsenic in fuels which is accurate, fairly rapid in execution, and which has the additional merit of directly distinguishing between the arsenic which is volatilised on burning the fuel and that which remains fixed in the ash. The process consists simply in burning a known quantity of the finely powdered coke or coal in a stream of oxygen, passing the products of combustion through a suitable absorbing apparatus, and determining the amount of arsenic so absorbed as well as that left in the ash.

The estimation of the arsenic in the solutions may be made by means of the Marsh apparatus and comparison with standard deposits of arsenic, or preferably with the electrolytic method described in the subsequent communication. The accuracy of the method was tested by burning fuels containing known quantities of arsenic, added in the form of arsenical pyrites.

*97. "*The Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials.*" By T. E. THORPE.

An electrolytic method for detecting arsenic appears to have been first suggested by the late Prof. Bloxam (*Quart. Journ. Chem. Soc.*, 1861, xiii., 12 and 338), but in its original form it had several disadvantages which have prevented it from being generally adopted by chemists. The process has been carefully investigated in the Government Laboratory, and in the form described in the present communication it is easy of application, and is capable of giving trustworthy results with a comparatively small expenditure of time and trouble.

The test may be applied to malt and malt substitutes, wort, hops, and hop substitutes, beer, yeast and yeast foods, finings, &c.

The advantages of the electrolytic method are:—

1. That it obviates the use of zinc.
2. It is simple in execution, is under perfect control, and may be carried out under such conditions that the results obtained by different operators are strictly comparable, inasmuch as with a current-strength of fair regularity the evolution of the gas is practically constant and uniform.
3. The whole of the solution to be tested for arsenic may be added to the apparatus at once, so that during the whole time of testing the arsenic is under the influence of the "nascent" hydrogen.
4. It has been established that such amounts of arsenic as are present in beer or its ingredients are evolved as hydrogen arsenide during the thirty minutes occupied by the test. The nature of the material associated with the arsenic is found to exercise no inhibiting effect on the

formation and evolution of the hydrogen arsenide. Aqueous extracts of malts and worts may be added directly to the electrolytic apparatus without previous destruction of the organic matter as required by the zinc and acid process.

5. The deposits obtained are more uniform in character than those furnished by the zinc and acid method, and admit therefore of more accurate quantitative comparison.

6. The process allows of the simultaneous execution of a number of estimations of arsenic, depending upon the arrangement of the rheostat.

The disadvantages of the method are :—

1. The initial cost of the apparatus as compared with that employed in the zinc and acid method.

2. That it can only be applied when an electric current of sufficient intensity is available.

DISCUSSION.

Dr. THORNE said the electrolytic process would prove of the greatest value to the large number of chemists who had to test for very small quantities of arsenic. The Marsh-Berzelius process was very reliable and accurate, and had been rightly recommended by the Committee of the Societies of Chemical Industry and Public Analysts, but those who used it knew the difficulty of obtaining zinc and hydrochloric acid free from arsenic, and hence these reagents must be carefully purified if the test was to be satisfactorily carried out. In the process just shown, these difficulties were obviated. He had had the opportunity of seeing the method in operation, and could therefore speak as to its satisfactory working.

Mr. ARTHUR R. LING also thought that the electrolytic process would doubtless prove much more convenient than the Marsh-Berzelius method, which, in the case of many materials, necessitated the destruction of organic matter.

In the set of standards exhibited, the mirrors obtained in the presence of glucose appeared to be less intense than those produced in the absence of organic matter, from the same weight of arsenic, by the Marsh-Berzelius method.

Mr. WILLIAM THOMSON believed that the electrolytic method suggested by Lord Kelvin and the ingenious apparatus devised by Dr. Thorpe and his colleagues may ultimately afford the most practicable means of detecting arsenic in beer and food-stuffs.

He had tested one of the appliances, and had found that it would not detect the presence of more than about 1/350th of a grain of As_2O_3 per gallon, whilst the zinc and acid method easily detects 1/1000th of a grain per gallon when using 50 c.c. of the solution. Assuming at first that this difference was due to an insufficient surface of cathode, he used a much larger area of platinum wire gauze, but obtained the same results with regard to the size of mirrors as those obtained in Dr. Thorpe's apparatus.

Platinum seems to retain minute quantities of arsenic, but when a pure zinc cathode is employed the 1/1000th part of a grain per gallon can easily be detected when using 50 c.c. of the solution.

He could confirm Dr. Thorpe's observations that minute quantities of arsenic in the form of pentoxide cannot be detected by the electrolytic method, 1/200th of a grain per gallon (using 50 c.c.) yielded no mirror at all with the platinum anode, and gave an approximately half-sized mirror with the zinc anode.

In other respects, his results differed from those obtained by Dr. Thorpe. He found that both amyl alcohol and sugar seriously reduce the size of the mirrors, and he was of opinion that it is unsatisfactory to test beer directly in Dr. Thorpe's apparatus.

Dr. MACGOWAN said that, together with Mr. R. B. Floris, he had during the past year examined a large number of samples of anthracite for arsenic. The method which, after some preliminary experiments, they had employed in this work was a modification of Newlands and Ling's basic process. Although the results obtained were very consistent, and, as they believed, accurate, yet this process had the disadvantage of being an indirect method with regard to the "volatile" arsenic present.

Other things being equal, a direct method such as that now brought forward by Dr. Thorpe was preferable.

Dr. THORPE, in reply to Mr. Ling, stated that he had not been able to perceive any difference in the intensity of the mirrors produced from a known quantity of arsenic in the electrolytic method as compared with the Marsh-Berzelius method. A comparison of the standards in the two cases, as shown on the table, would prove that there was no practical difference in the two series.

In reference to what fell from Mr. Thomson, he might say that attempts had been made to increase the activity of the cathode by depositing platinum black upon it, but nothing seemed to be gained thereby. Experience showed that the best and most uniform results were obtained by keeping the metallic surfaces as clean and bright as possible.

*98. "Crystallised Ammonium Sulphate and the Position of Ammonium in the Alkali Series." By A. E. H. TUTTON.

The author has hitherto shown that the morphological and physical properties of the crystals of the normal sulphates and selenates of potassium, rubidium, and caesium follow the order of progression of the atomic weights of the three alkali metals. An analogous study of normal ammonium sulphate indicates that this salt stands in the series of normal alkali sulphates between rubidium and caesium sulphates, and very close to the rubidium salt, as regards the following nine properties:—Solubility, molecular volume, distance ratios (topic axes), refractive indices, axial ratios of the optical ellipsoid, molecular refraction along axial directions, mean refraction equivalent both for the crystallised and the dissolved salt, and the general optical scheme which governs the optic axial angle phenomena. With respect to all these properties, the replacement of the two atoms of potassium by the ten atoms composing the two NH_4 groups is accompanied by an effect but slightly greater than when two atoms of rubidium are substituted for those of potassium.

The specifically different nature of the ammonium radicle as compared with a metallic atom of the alkali group asserts itself in regard to the morphological angles and axial ratios, the specific refraction, certain details of the distance ratios and the optic axial angle phenomena, and in the development of only one instead of two cleavages. Yet even in the case of the crystallographical angles, this difference is only manifested with regard to the direction of the change of angle on replacement, and as far as the amount of change is concerned the ammonium compound stands between the rubidium and caesium salts, and somewhat nearer to the latter. It is, indeed, surprising that the introduction of eight additional atoms should be accompanied by less change in the exterior angles of the crystals than when an exchange of caesium for potassium atoms occurs.

In short, the specific constants indicate the peculiar nature of the ammonium radicle, whilst the molecular constants show that ammonium occupies a place in the alkali series immediately after rubidium.

This result opens up questions of the arrangement of the atoms in the molecule, and the closeness of the packing of the molecular structural units in the crystal edifice. It suggests that either the atoms have a range of motion inside the molecular dimensions sufficiently wide to admit eight more atoms without altering those dimensions to an appreciably greater extent than when the transposition of rubidium and potassium atoms is effected, or that the structural units are so loosely packed, that is, the amount of free space is so large as compared with the amount of matter in the whole space defined by the distance ratios, that there is adequate room for the increase of the material part of the molecule by eight atoms, without separating the centres of contiguous molecules more than when a simple metallic interchange occurs.

*99. "The Action of Hydrogen on Sodium." By A. HOLT, jun.

Pieces of sodium free from oil were placed in a nickel boat and heated in a combustion tube through which a slow current of pure dry hydrogen was passing. An ordinary small combustion furnace without top tiles was employed, and it was arranged so that, whilst the lower part of the tube was strongly heated, the upper portion was kept at a lower temperature in order that the hydride might condense on it. The hydride thus obtained consisted of colourless matted crystals, a hairy deposit not unlike cotton-wool, and a white powder deposited next to the glass. The hairy material was formed on and above the powder in front of the boat, whilst the crystals projected from the surface of the tube at either side of the boat.

The analysis was performed (1) by decomposing the hydride with dry, air-free hydrogen chloride, collecting the hydrogen due to the reaction, and estimating the sodium chloride formed by titration with silver nitrate; (2) by decomposing the hydride with absolute alcohol, collecting the hydrogen evolved, and estimating the sodium in the alcoholic solution by titration with standard acid. The ratio of sodium to hydrogen showed that the hydride had the composition NaH, as already stated by Moissan.

The hydride was instantly decomposed by water, forming sodium hydroxide and hydrogen, this result also occurring in air after a few minutes; it was at once decomposed by hydrochloric acid, the decomposition being accompanied by flame and a detonation. The hydride was immediately attacked by nitric and sulphuric acids, hydrogen sulphide, and alcohol, but ether, benzene, and mercury were without action on it.

With phenol and ammonia, it reacts only when heated, forming sodium phenoxide and sodamide respectively.

Carbon dioxide, when perfectly dry, has no action on the hydride at the ordinary temperature, but on heating, a reaction takes place with the formation of carbon and a carbonate. The partially dried gas reacts with the hydride at the ordinary temperature, yielding a formate and carbon. When heated with ferric oxide, the hydride gives a ferrate.

The combination of hydrogen with sodium appears to take place only when the latter is in a state of vapour; the sodium probably interacts only when it is partially monatomic.

100. "The Action of Halogens on Compounds containing the Carbonyl Group." By ARTHUR LAPWORTH.

Although bromine acts very slowly on a dilute aqueous solution of acetone, yet, in presence of alkali, bromination occurs readily. It is now found that acids also accelerate the speed of substitution to an extent which depends mainly on the concentration of the hydrogen ions, although the nature of the anion appears to have some influence.

In the author's experiments, the concentration of the bromine was always considerably less than that corresponding with one molecular proportion, and at constant temperature the velocity with which the bromine disappeared was nearly independent of its concentration. With sulphuric acid between the concentrations 0.4 N and 0.04 N, the velocity increased somewhat less rapidly than the concentration of the acid, but slightly more rapidly than that of the acetone. The relative velocities of reaction with 0.4 N sulphuric, nitric, and hydrochloric acids were about 1:19:1:20:1:36. The velocity was not affected if the acetone was left in contact with the dilute acid for several days before the introduction of the bromine.

Preliminary experiments with chlorine indicate that in presence of much acid it is removed at about the same speed as bromine.

These facts confirm the view that the bromination is not a process of direct substitution, but is preceded by a reversible change of the acetone, accelerated by acids or alkalis, to a second form, probably the enol, this modification being brominated nearly instantaneously. It has already been shown that in many cases acids promote the attainment of equilibrium between *ketonic* and *enolic* modifications (*Trans.*, 1902, lxxi., 1500, and *Proc.*, 1903, xix., 149).

The action of acids in accelerating substitution is not confined to aqueous solutions, but may be readily followed in other solvents.

The action of bromine and chlorine on other carbonyl compounds, as, for example, malonic ester and acetic anhydride, is greatly accelerated by acids. Even dry acetic acid is readily converted into its mono-bromo-derivative on the water-bath if it is first saturated with hydrogen chloride or bromide. The latter observation explains the action of a small quantity of phosphorus or phosphorus halogen compounds in promoting the action of chlorine and bromine on carboxylic acids, and the introduction of a suitable amount of the acid chloride appears equally effective when the acid contains water.

101. "Reactions involving the Addition of Hydrogen Cyanide to Carbon Compounds." By A. LAPWORTH.

In order to ascertain the conditions under which hydrogen cyanide is most rapidly taken up by carbon compounds, camphorquinone was brought into contact with that substance in the presence of different agents which might possibly influence the reaction velocity, a rough measure of the latter being obtained by noting the speed with which the colour of the quinone disappeared.

The reaction, which was very slow in aqueous solution and was retarded by acids, was extremely rapid in presence of strong bases, and was accelerated by salts of weak acids. This result indicates that the change is effected by the cyanogen ions, a view confirmed by further experiments.

The great additive power of "nascent" hydrogen cyanide as compared with that of the agent in the free state is now readily understood, as the former occurs in presence of potassium cyanide.

When the addition product is fairly stable towards alkalis, it is not necessary actually to liberate the hydrogen cyanide. Camphorquinone may, in a few seconds, be largely converted into its cyanohydrin by shaking with a concentrated aqueous solution of potassium cyanide. Benzylidene benzylcyanide gives more than 30 per cent of the theoretical amount of diphenylsuccinonitrile if warmed for twenty minutes in alcoholic solution with excess of potassium cyanide, although it does not appear to unite with hydrogen cyanide in the absence of its salts; phorone is rapidly converted into phoronitrile under the same conditions.

With potassium cyanide, benzaldehyde yields mandelonitrile. The latter compound condenses with the former in presence of bases to yield hydrogen cyanide and benzoin. The well-known benzoin condensation may therefore be represented as the result of the formation of the unstable cyanohydrin of benzoin by the ordinary addition process,—

$\text{CHPh(OH)·CN} + \text{PhCHO} = \text{OH·CPh(CN)·CHPh·OH}$,
where the mandelonitrile behaves as the hydroxy-derivative of benzyl cyanide, a substance which is known to condense readily with benzaldehyde.

(To be continued).

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

THE above Society met on Monday evening, June 22nd. Dr. C. E. FAWSITT in the Chair. Papers were read by Dr. Drinkwater and Dr. Hugh Marshall. There was a large attendance.

Dr. DRINKWATER's paper was on "Distillery Residues." He gave a description of the waste products produced in both grain and malt distilleries, and showed the manurial and feeding values of some of these products and their polluting effect when put into running streams. The vacuum methods which had been adopted during the last few years for dealing with these residues, and the results of experiments in filtering and treatment by septic tanks, were also discussed. He concluded by saying that he was in favour, on the whole, of evaporating the residue under suitable conditions, and using it as a manure.

The title of Dr. MARSHALL's paper was "*The Use of Carburetted Air for Lighting and other Purposes.*" In it he described and showed various lamps for burning carburetted air, prepared by passing ordinary air over blocks of absorbent material saturated with petrol or other highly volatile hydrocarbon mixtures. In some of these the supply of vapour to the burner is effected by gravity, but in others, more recently devised, the draught of the burner-tube draws the vapour from a carburetter placed below the burner proper. He also described improved arrangements for installation in country houses, by which a supply of carburetted air could be led over the house like an ordinary gas supply, and used for lighting, heating, &c.

NOTICES OF BOOKS.

An Index to the Complete Encyclopædia Britannica; being the Eleventh of the New Volumes which constitute in conjunction with the Existing Volumes of the Ninth Edition, the Tenth Edition of that Work. Vol. XXXV. of the Complete Work. Edinburgh and London: Adam and Charles Black; and *The Times*, Printing House Square. 1903. Pp. 1092.

WITH this volume we see the completion of the task undertaken by the Editors three and a-half years ago. The magnitude of such a work has necessarily taxed the energies of the Editorial Staff and their assistants to the utmost, but in spite of certain objections and protests that have been raised as to the somewhat strong American flavour of the work, there can be no denying the fact that this edition of the *Encyclopædia Britannica* reflects the highest credit on everyone concerned in its production.

It is hardly to be expected that special subjects, such as chemistry, physics, electricity, and the cognate sciences, could be dealt with in the same thorough manner as in the literature devoted entirely to these matters: still, although the space allotted to Science has been small in comparison with that devoted to other subjects, the materials have been supplied by the highest authorities in each special branch, and to the casual reader, whose interest is not that of a student, the articles will be found interesting and sound so far as they go. The great bulk of this work will prevent its acquisition by the small householder, but by the general public who can avail themselves of the numerous Public Libraries now springing up with such vigour all over the country, it will be found useful as a book of reference on practically every subject under the sun.

Fermentation Organisms; a Laboratory Handbook. By ALB. KLÖCKER. Translated from the German by G. E. ALLAN, B.Sc., and J. H. MILLAR, F.I.C., and Revised by the Author. With 146 Illustrations in the Text. London, New York, and Bombay: Longmans, Green, and Co. 1903. Pp. 392.

ALTHOUGH there are many books dealing with the micro-organisms of disease, it must be admitted that we have not been well supplied with works dealing with microbiology from the opposite point of view, viz., the micro-organisms which are serviceable or even necessary to man, and this is especially the case with regard to the more modern developments connected with the study of these organisms. It is for this reason that we welcome the publication of the present volume, which deals most thoroughly with the subject of fermentation organisms.

The book is divided into three sections, the first of which is introductory and covers a few pages only.

Section II. is on "The Laboratory," and deals in a minute and comprehensive manner with all the latest apparatus and instruments for the proper fitting-up of a modern bacteriological laboratory. It is assumed, of course, that the reader is not a beginner, but has already acquired some familiarity with bacteriological methods.

But it should not be overlooked that though the broad principles of manipulative bacteriology do not vary, every writer has his own special methods, and many a useful dodge can be picked up from new publications.

In a subject such as the present one, where the preparation of pure cultures is so important, too great stress cannot be laid on the necessity for guarding against the intrusion of foreign germs. The precautions to be taken, and the various methods of sterilisation and culture, are all fully dealt with in this section.

Section III. deals with the micro-organisms of most importance in the fermentation industry; these organisms are, of course, partly useful and partly disadvantageous to the alcohol industry. They are all members of that branch of the plant kingdom called fungi, and here we find a review of the systematic connection of the micro-organisms to be described.

Yeast, which is the most important organism in connection with the brewing industry, belongs to the genus "*Saccharomyces*"; these are divided again into six species, according to which of the sugars, maltose, dextrose, lactose, saccharose, &c., they do or do not ferment. The systematic study of these organisms covers a good many pages. In this section we find also the inimical or disease organisms of fermentation; they are all treated in the same systematic manner as the others. It is not easy, in the compass of a short review, to give an adequate idea of the scope of this volume, not of the care with which it has been prepared. We look upon it as a valuable contribution to the literature of micro-organisms, and feel sure that it will be read with both pleasure and profit, not only by the younger students, but by those who have already given much time and attention to this important subject.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band III. 12 Heft. Edited by FRANZ HOFMEISTER. Braunschweig: Friedrich Viewig und Sohn. 1903.

THE April number of this journal brings to a conclusion the third volume, and contains the index to the papers which have appeared in it. This number contains only three articles; the most important from a chemical point of view being, perhaps, the third, on the autolysis of the lymph glands. The author of this paper, A. Reh, has proved the formation of ammonia, leucin, tyrosin, thymine, and uracil; thus partly confirming results which have been previously obtained by other investigators, and also adding to them, as in the case of uracil, which has not been detected before, among the products of the autolysis of the lymph glands. In the long paper on the coagulation of the albuminous substances of muscle, and their supposed connection with muscle rigor, a particularly exhaustive research into the subject is described, with the details and results of many experiments.

Die Aluminium-Industrie. ("The Aluminium Industry"). By Dr. F. WINTELER. Braunschweig: Friedrich Viewig und Sohn. 1903.

THE author of this work, feeling that up to the present most of the books published on such subjects as the above have been too much occupied with the repetition of lists of patents, has endeavoured to produce a convenient work for the use of students and technical men, who require more information on the actual methods and processes employed than on the details of the advance of our knowledge of the more purely scientific aspect of the subject. Thus he has excluded all that is useless from a practical point of view, and aimed at supplying the want of the means of obtaining trustworthy details as regards the preparation, &c., of aluminium on a large scale in a convenient form. The result is eminently satisfactory, and the book fulfils its purpose admirably. The properties of

the metal, both physical and chemical, are given in full, and modern methods of analysis are included in a section, which, though succinct, is quite sufficiently detailed. The book concludes with the description of the applications and uses of aluminium, and the preparation and properties of some of its alloys.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 22, June 2, 1903.

Cementation of Steels.—Léon Guillet.—The author's researches on the cementation of steel show—(1) That the rapidity of penetration of carbon into the steel depends on the temperature, the time, and the chemical reactions produced by the carbon; (2) the experiments made did not determine the solubility of the carbon in the iron, but they apparently establish the fact that there is a preliminary state of equilibrium which is destroyed by the final operation; (3) by simple cementation certain steels containing nickel acquire the same hardness as carbon steels.

The Form in which Mercuric Iodide goes into Solution.—D. Grenet.—The author shows that the vapours emitted by red quadratric mercuric iodide at temperatures below the transformation-point (126° under atmospheric pressure) take the yellow orthorhombic form on condensation. He further investigates the form in which mercuric iodide goes into solution, and comes to the conclusion that the two changes of state of red mercuric iodide, either when volatilised or when dissolved, cause the body to be transformed into the unstable yellow variety, even when the transformation takes place at temperatures at which the red iodide is in its most stable state.

Precipitation of Manganese by Persulphuric Acid in Acid Solution.—H. Baubigny.—This paper gives an account of the further researches by the author on the precipitation of manganese by persulphuric acid, when various changes take place in the relative acidity of the solution and of the absolute mass of free H_2SO_4 as compared with the weight of the manganese.

Alloys of Copper and of Magnesium.—O. Boudouard.—The author investigates the relation between the fusibility and the physical and mechanical properties of the alloys of copper and magnesium. The curve of fusibility shows the existence of three definite compounds— Cu_2Mg , CuMg , and CuMg_2 . Constants obtained by microscopic metallography and chemical analysis confirm the existence of these definite compounds.

Chromium Silicides.—P. Lebeau and J. Figueras.—The action of silicon on a metal in presence of copper allows of the preparation of the definite compounds which silicon forms with iron, cobalt, and manganese. The method consists in reacting on a mixture of copper and of the metal with varying proportions of silicon in the form of siliciuretted copper, free silicon, or silicon obtained from the action of sodium on an alkaline fluosilicate. By applying these methods to the binary combinations of chromium and silicon, the authors succeed in isolating the four chromium silicides, SiCr_3 , SiCr_2 , Si_2Cr_3 , Si_4Cr .

Electrolytic Reduction of Incomplete Acids.—C. Marie.—The author's researches on the electrolytic reduction of incomplete acids show that the double ethylenic liaison is capable of fixing a hydrogen atom during electrolysis. In the case of bodies which are easily oxidised this property prevents their electro-chemical oxidation; it also

prevents the necessity of the preparation and somewhat difficult application of sodium amalgam.

Dibromo-acetylene, $\text{CBr}\equiv\text{CBr}$.—P. Lemoult.—The author succeeds in preparing dibromo-acetylene and identifying it by certain characteristic properties. The principle of the preparation consists in transforming two molecules of HBr into symmetric tetrabromomethane, $\text{CHBr}_2\text{—CHBr}_2$. This transformation is attended by many difficulties, because the body obtained is spontaneously inflammable in air, is decomposed by heat, and is explosive. It is a colourless liquid of density 2; it is incapable of being distilled without decomposition even *in vacuo*; its boiling-point is about 80° ; and it is soluble in the majority of organic solvents.

MISCELLANEOUS.

On Terbium.—R. Marc.—Oxide of terbium has a very marked brown ochre colouration. That which has been described previously was nothing better than a mixture of yttria with other heavier earths, which were colourless, and had no absorption spectrum (ytterbium, no doubt), and were coloured by a little terbium. Terbium has two degrees of oxidation; a lower, coloured oxide, and a colourless peroxide (as with praseodymium). Its absorption spectrum appears to be characterised by a band, $\lambda = 464\text{—}461$. Its atomic weight is about 157.—*Berichte*, vol. xxxv., p. 2382.

Soluble Salts of Manganese.—Recent experiments have afforded increased evidence that manganese possesses useful qualities in the treatment of debilitating diseases associated with anæmia. It appears, however, that the nature of the combination in which the manganese is employed exercises an important influence upon the therapeutic effects. Some experiments conducted in the Wellcome Chemical Research Laboratories, with a view of preparing a soluble salt of manganese of a stable character, have proved highly satisfactory. As a result of these investigations Messrs. Burroughs, Wellcome, and Co. are manufacturing a soluble citrate of manganese, as well as two soluble compounds of manganese and iron.

The Determination of the Principal Impurities in Anthracene.—H. Behrens.—For the detection of carbazol in anthracene the latter is exhausted with acetic ether; the solvent is allowed to evaporate, and the residue taken up again with a few drops of the same liquid; after evaporation on a watch-glass a residue is obtained, of which the centre consists of anthracene and the periphery of carbazol. A little of this latter substance is dissolved in a drop of nitrobenzene treated with a little phenanthrenequinone; the presence of carbazol causes the appearance of copper-coloured tablets. In the case of phenanthrene, we substitute benzene for the acetic ether, and the characterisation is done by means of α -dinitrophenanthrenequinone in nitrobenzene.—*R. Tr. Ch. P.-B.*, No. 2 and 3, p. 252.

Thallous Sulphates.—W. Stortenbeker.—The presence of 1 to 2 molecules of H_2SO_4 for each one of Tl_2SO_4 dissolved in water helps the crystallisation; much larger crystals are obtained. One molecule of Tl_2SO_4 is soluble at 18° in 600 molecules of water, and, on the other hand, in 193 molecules of water treated with 9.4 molecules of H_2SO_4 ; this latter solution, after being concentrated down to one-half, deposits an acid sulphate of thallium, $(\text{SO}_4)_2\text{Tl}_3\text{H}$, or $\text{SO}_4\text{Tl}_2\cdot\text{SO}_4\text{HTl}$, in pearly hexagonal flakes. By concentrating the acid solution of SO_4Tl_2 strongly on the water-bath, the author obtained the acid sulphate, SO_4HTl , in square hygroscopic plates, fusible at $115\text{—}120^{\circ}$; this salt appears to be dimorphous; in fact, we find prismatic orthorhombic needles, along with these clinorhombic plates.—*R. Tr. Ch. P.-B.*, vol. xxi., No. 1, p. 87.

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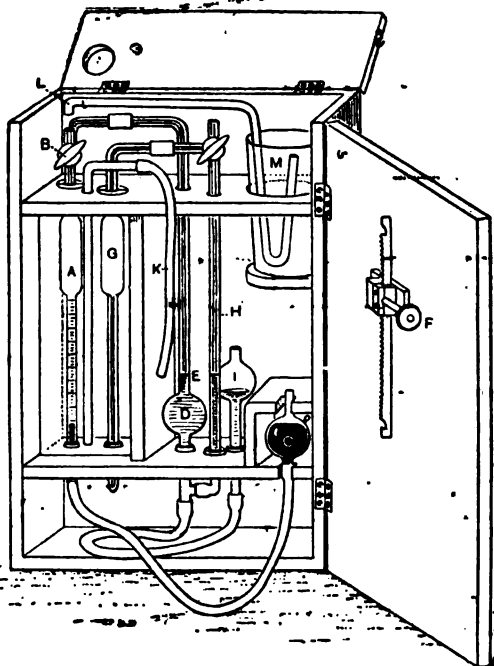
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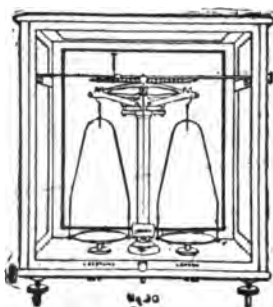
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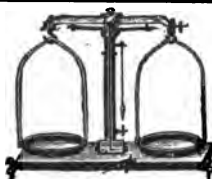
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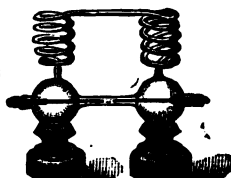
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2276.

ON THE ATOMIC WEIGHT OF LANTHANUM.

By HARRY C. JONES.

In a recently described determination of the atomic weight of lanthanum, Brauner and Pavlicek (*Amer. Chem. Journ.*, 1902, xxviii., 23) found the value 139.04. A careful examination of their paper shows that a large amount of painstaking work was done, and great care was exercised in certain directions. Their value, however, differed from my own by a little more than a quarter of a unit (*Journ. Chem. Soc.*, lxxxi., 1243).

It was obvious, therefore, that there must be some hidden source of error in at least one of the series of determinations, and possibly in both.

Work was undertaken with the object of determining, if possible, the cause of the difference between the values found by Brauner and those obtained in this laboratory.

An examination of the paper by Brauner and Pavlicek, which was not published in full until after the appearance of my own, convinced me that, notwithstanding the fact that they had undoubtedly taken very great care in certain directions, in other directions their work contained possible sources of error. Their own rather sweeping criticism of a large number of investigations by careful workers, near the close of their paper, viz., "*all atomic weight determinations of the rare earth elements made by the synthetical sulphate method during the nineteenth century are vitiated by an error which tends to lower the atomic weight and diminishes as the basicity of the earth decreases.*" seemed to me not to be sufficiently substantiated by experiment. This would probably depend upon the temperature to which the sulphate had been heated, and also the time during which it was heated, free access of air, &c. This point was very carefully tested in my earlier work, using methyl orange as the indicator, and *not the slightest trace of acidity* could be detected.

Quite recently a criticism of my work by Brauner has appeared, in which a number of points are raised (*Zeit. Anorg. Chem.*, 1903, xxxiii., 317). He thinks that my material was not sufficiently free from cerium, after I had stated that "The oxalate was then decomposed to the oxide and analysed spectroscopically by Mr. L. E. Jewell, whose work in this field is so well known. The only impurity which could be detected was a trace of cerium, and this was not more and probably much less than 0.01 of 1 per cent." This analysis was made by means of the large Rowland spectroscope, by one of the most expert spectroscopists living, and I therefore think the results can be accepted, notwithstanding Brauner's opinion to the contrary. A moment's thought would, however, convince any one that traces of cerium would produce a negligible influence, since the atomic weight of cerium is so close to that of lanthanum.

Brauner's suspicion that in my determinations some of the oxide was lost by spattering, would have been removed by carefully reading what was stated on this point.

The various other points referred to by Brauner are matters which would be looked after and guarded against by any one in an ordinarily careful quantitative analysis, and still more, of course, in an atomic weight determination, and there seemed to be no occasion on my part to refer to them in print.

Possible Sources of Error in the Work of Brauner.

I was particularly impressed in reading the paper by Brauner and Pavlicek with the fact that they heated the oxide of lanthanum in a platinum crucible placed inside

another platinum crucible. They themselves state that the oxide in "contact with the hot walls of the platinum crucible assumed an extremely slight pale buff tint. This tint was slightly more prominent in the higher fractions."

In my own work, I at first had used this same method for heating the oxide to constant weight. I had also observed that the oxide next to the platinum became coloured, and immediately abandoned the platinum crucibles altogether, and adopted porcelain crucibles in their stead. I supposed that the change in colour indicated a change in the composition of the oxide—a supposition which we shall see later is made highly probable.

Brauner determined the amount of acid sulphate in his product by titration with a standard alkali, and introduced the corresponding correction. It is difficult to see how he knew the composition of the acid sulphate which was present in such very small quantities. This, of course, could not be assumed from the composition of the acid sulphate prepared under different conditions.

One reads Brauner's paper in vain for an account of a thorough spectroscopic study of the material which he used in his work. This does not refer to a study of the absorption spectrum, since many substances do not yield characteristic absorption spectra, but to a careful examination of the emission spectrum. Certainly no material should be used to-day for atomic weight work, whose emission spectrum had not been carefully photographed, and the proper comparisons made to determine the presence or absence of foreign substances. This is especially desirable in the case of the rare earths, where, on account of the unusual similarity in the chemical properties of the substances, chemical methods are not capable of detecting traces of impurities, if these impurities are the other rare earths. I do not doubt that the Rowland spectroscope would have convinced Brauner that his lanthanum contained at least traces of impurities, and that he was not dealing with absolutely pure material.

One other point in connection with the work of Brauner and Pavlicek seems to call for special comment. They state (*Journ. Chem. Soc.*, 1902, lxxxi., 1252): "On heating the salt (lanthanum sulphate) to a temperature which in some cases may have finally exceeded 600°, that part which adheres to the platinum walls of the crucible may become partly converted into the basic salt, that part which lies nearer the centre may consist of the normal salt, and the uppermost inner layer may consist of some incompletely decomposed acid sulphate."

This would show that the sulphate was not heated uniformly throughout; the outer layer being heated to the highest temperature, the middle layer less highly heated, while the innermost layer was still less strongly heated. This is quite explicable when we consider the arrangement used by Brauner and Pavlicek for heating the sulphate. They state (*Journ. Chem. Soc.*, 1902, lxxxi., 1250) that "the platinum crucible was fastened in the centre of a large porcelain crucible, having in its lid a thermometer graduated up to 550°, by which, at least, the order of the temperature was indicated. The large crucible fitted into a larger plate of asbestos cardboard, in order to exclude the products of the combustion of coal."

Under the above conditions, with such a small air-space around the platinum crucible, it is obvious that the sulphate would be heated to a temperature which grew less and less as the distance from the platinum walls increased, and the temperature indicated by the thermometer suspended in the air in the innermost crucible may have borne no very close relation to the temperature of the lanthanum sulphate in contact with the platinum. The thermometer would, obviously, have indicated a considerably lower temperature than that to which the outer layer of lanthanum sulphate was subjected, and have given no clue to the correct temperature of the sulphate in contact with the platinum. This is shown by the fact that the outer layer of sulphate was partly decomposed into basic sulphate, while the inner layer still contained some acid sulphate.

Some New Determinations of the Atomic Weight of Lanthanum.

I determined to repeat my earlier work on the atomic weight of lanthanum, taking even greater precautions in heating the substances and preserving them in the dry condition until weighed. It was thought that in the repetition of the work possibly some sources of error might appear which had been overlooked. The oxide was highly heated over the blast-lamp in a porcelain crucible, and was perfectly white. It was transferred red-hot to a desiccator containing fresh phosphorus pentoxide, and allowed to cool over the pentoxide. It was finally weighed in the platinum crucible in which the determination was to be made, the platinum crucible and oxide being enclosed in a ground-glass stoppered weighed tube. The remaining operations in connection with the synthesis of the sulphate were essentially the same as in the first series of determinations. The sulphate was always weighed in the platinum crucible, which was placed, while hot, in a ground-glass stoppered weighing tube, and the whole allowed to cool in a desiccator over fresh phosphorus pentoxide. Special care was taken to test for the presence of acid sulphate, using methyl orange. A given number of drops of the indicator was added to the solution of lanthanum sulphate, and an equal number to an equal volume of pure, re-distilled water. The water used to dissolve the lanthanum sulphate, and for comparison, had been distilled from chromic acid and then from barium hydroxide, and had a conductivity of 1.2×10^{-6} .

The two tubes—the one containing the lanthanum sulphate and the indicator, and the other the pure water and the indicator, were then passed around the laboratory to the several instructors and advanced workers, with the request for them to decide which solution showed an acid reaction. In no case could any difference be detected by any one.

The question of the solubility of the lanthanum sulphate in pure water was then carefully tested in each experiment. The sulphate dissolved at once, on coming in contact with the water, and manifested none of the behaviour described by Brauner and Pavlicek (*Journ. Chem. Soc.*, 1902, lxxii., 1252). This convinced me that Brauner and Pavlicek were justified in concluding that their sulphate was not homogeneous, and that the cause of the heterogeneity of their material was, as already suggested, that the sulphate was heated in an air-bath which was too small to permit of a uniform heating of the salt.

Results.

The results of five determinations are given below:—

	La_2O_3	$\text{La}_2(\text{SO}_4)_3$	$3\text{SO}_3=240.18$	At. wt. La.
I.	1.2161	2.1132	0.8971	138.79
II.	1.6311	2.8342	1.2031	138.81
III.	1.7804	3.0938	1.3134	138.79
IV.	1.4168	2.4619	1.0451	138.80
V.	1.9702	3.4235	1.4533	138.80

Average = 138.80

The average of these results, 138.80, differs from the mean of my first ten determinations—138.77—by an amount not larger than the possible experimental error (*Amer. Chem. Journ.*, 1902, xxviii., 33).

Determination of the Atomic Weight of Lanthanum when the Oxide is Heated in Platinum.

Having found essentially the same value for the atomic weight of lanthanum in this series of determinations as in the earlier series, it occurred to me to make a determination or two, heating the oxide in one platinum crucible placed inside of another platinum crucible, as Brauner had done. The two platinum crucibles were separated by a small piece of asbestos paper to avoid any tendency for them to stick together when heated over the blast-lamp. In the first of the following determinations the oxide was heated for two

hours in platinum. Although the oxide remained perfectly white when heated in porcelain for any length of time, when heated in platinum in the manner above described, it showed a marked tint, especially next to the walls of the platinum where it had been most highly heated.

In the second determination, recorded below, the oxide was heated in the platinum crucible for five hours, and showed deeper coloration than the oxide that had been heated a shorter time.

	La_2O_3	$\text{La}_2(\text{SO}_4)_3$	$3\text{SO}_3=240.18$	At. wt. La.
I.	1.2820	2.2264	0.9444	139.02
II.	1.3885	2.4110	1.0225	139.08

The results thus obtained are not only higher than those found in my work, but differ appreciably as the time during which the oxide of lanthanum was heated in the platinum was increased.

The higher value found would indicate that the lanthanum oxide had undergone slight oxidation in the platinum. This was tested by transferring the oxide which had been heated in platinum for several hours to a porcelain boat, inserting the boat into a large tube of hard glass through which a current of hydrogen was passed, and heating the tube on a combustion furnace. The oxide, under these conditions, lost in weight. A loss as great as 0.002 grm. per grm. of oxide was detected when the oxide was heated in a current of hydrogen for from one to two hours.

In the very first stages of my work on the atomic weight of lanthanum, I heated the perfectly white oxide, obtained by decomposing the oxalate and heating the resulting oxide in porcelain, in a current of hydrogen to a bright-red heat for two hours, without being able to detect the slightest loss in weight. It is, of course, absolutely essential in this work that under the above conditions there should be no loss in the weight of the oxide, otherwise it would be very probable that we were dealing with the sesquioxide containing a small amount of a higher oxide of lanthanum.

In my opinion, the above facts account satisfactorily for the difference between Brauner's result and my own. If Brauner will heat his oxide only in porcelain, and not in platinum, he will obtain a lower value for the atomic weight of lanthanum. In reference to the atomic weight of praseodymium it is almost superfluous to repeat what has already been said. The question of the presence of both acid and basic salts was carefully considered (*Amer. Chem. Journ.*, 1898, xx., 353), and the result recorded five years ago. Notwithstanding this fact, Brauner and Pavlicek (*Journ. Chem. Soc.*, 1902, lxxii., 1249) state that:—"No one, however, has considered the other side of the question, How can we find out whether the sulphate does not contain an excess of sulphuric acid?" The mean of my results, 140.46, agreed so well with that found simultaneously by von Scheele (*Zeit. Anorg. Chem.*, 1898, xvii., 310), working with Clève, 140.40, that further work along this line seemed superfluous to both von Scheele (*Ibid.*, 1901, xxvii., 57) and myself. This was especially the case when we considered that the two pieces of work were done with entirely different material, obtained from very different sources, purified in different ways, and the determinations, although carried out by essentially the same method, must have involved very different details in the manner of heating the oxide and sulphate. The temperatures to which these substances were heated in the two sets of determinations were probably quite different, and might have been very different.

When we consider all of these facts the agreement between the results of von Scheele and my own is really quite remarkable, and makes it highly probable that objections such as those urged by Brauner are untenable. If such objections were really valid it is almost inconceivable that they should have affected the two sets of determinations in exactly the same way and to exactly the same extent in every case.

Brauner's value for the atomic weight of praseodymium differs from that of von Scheele and my own by about one-half a unit. Brauner's value for the atomic weight of

neodymium in one series of determinations is nearly identical with my value. In another series it is about 0.2 of a unit higher. Unless these differences can be explained on the same ground as in the case of lanthanum, no satisfactory explanation has yet been furnished.

Johns Hopkins University,
April, 1903.

CYANOGENESIS IN PLANTS.*

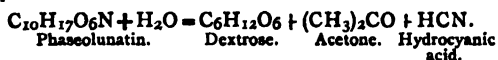
PART III.—PHASEOLUNATIN; THE CYANOGENETIC GLUCOSIDE OF *Phaseolus lunatus*.

By WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Imperial Institute, South Kensington,

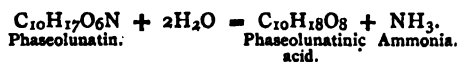
and
T. A. HENRY, D.Sc., London.

Phaseolus lunatus is an annual plant probably indigenous to South America, but now generally cultivated throughout the tropics for the sake of its nearly white edible bean, often known as the "Lima" or "Duffin" bean. In Mauritius the plant is grown under partial cultivation for use as a green manure, and produces under these conditions beans which differ from those obtained under thorough cultivation, in exhibiting dark brown or purple seed coats, and in being more or less poisonous. The poisonous properties of these beans have been shown by M. Bonamé ("Rapport Annuel de la Station Agronomique de Mauritius," 1900, p. 94) to be due to the production of hydrocyanic acid, which is formed when the crushed beans are moistened with water. Subsequently van Romburgh (*Annales de la Jardin botanique de Buitensorg*, Series II., vol. i., p. 2) verified this observation and showed that acetone was simultaneously formed.

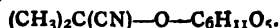
In continuation of our investigation of the production of prussic acid by plants, we have further investigated this subject. The seeds of *Phaseolus lunatus*, collected in Mauritius through the kind offices of M. Bonamé, have been found to contain a cyanogenetic glucoside, which has been named phaseolunatin. This glucoside crystallises in colourless needles, is readily soluble in water, and is laevorotatory in solution. Its composition is expressed by the formula $C_{10}H_{17}O_6N$. When hydrolysed by emulsin or by boiling with dilute acids, it is converted into acetone, dextrose, and hydrocyanic acid, according to the equation—



When warmed with alkalis, phaseolunatin is converted by hydrolysis into phaseolunatinic acid, and this acid, by the further action of dilute acids, is decomposed into dextrose and α -hydroxyisobutyric acid. These two reactions are represented by the following equations—



These observations prove that phaseolunatin is the dextrose ether of acetonecyanhydrin, and that its constitution is represented by the formula—



Phaseolunatin is, therefore, the first member of a new class of natural cyanogenetic glucosides since it contains an aliphatic nucleus; amygdalin, dhuririn, and lotusin, the other known cyanogenetic glucosides, being aromatic compounds.

The enzyme present in the seeds of *Phaseolus lunatus* has been examined and shown to be identical in its properties and in the effects it produces with the emulsin of almonds.

Specimens of the so-called "Rangoon" or "Paigya" beans derived from *Phaseolus lunatus*, grown in India and imported into this country for the manufacture of cattle food, have also been examined and shown to contain a small quantity of phaseolunatin. The amount of hydrocyanic acid producible from the seeds of *Phaseolus lunatus* has been found to vary from 0.041 per cent in the case of light brown beans, to 0.088 per cent in the case of dark brown or purple beans. The specimens of "Rangoon" beans examined furnished on an average about 0.004 per cent of this acid.

The authors draw attention to the fact that under cultivation this plant furnishes light coloured or white beans, which are incapable of producing prussic acid, and contain no phaseolunatin, although the enzyme emulsin is still present. In this respect the seeds of *Phaseolus lunatus* resemble those produced by the two varieties of almond (*Prunus amygdalus*). The bitter almond contains both the cyanogenetic glucoside, amygdalin and the enzyme emulsin, while the sweet almond contains emulsin only.

Treub (*Annales de la Jardin botanique de Buitensorg*, 1895, vol. xiii., p. 1) has suggested that in the case of *Pangium edule*, the at present unknown precursor of prussic acid in this plant may play the part of a formative material in the synthesis of amides and proteids. This is also probably true of the cyanogenetic glucosides which the authors have isolated from *Lotus arabicus*, *Sorghum vulgare*, and *Phaseolus lunatus*. The absence of phaseolunatin from the seeds of the cultivated *Phaseolus lunatus* and of amygdalin from those of the sweet almond, which there is reason to believe is the cultivated variety of *Prunus amygdalus*, may be the result of the more active metabolism induced by improved nutrition and environment, which leads to the more rapid utilisation of the glucosides by the cultivated plant, so that no supply of these substances is available for storage as reserve materials in the seeds.

EXPERIMENTAL DETERMINATION OF EQUIVALENTS.

By JOHN BRIDGEFORD COPPOCK, F.I.C., F.C.S.

THIS method consists in using the inner tube of a Lothar Meyer's vapour-density apparatus. It lends itself to a lecture table method of determining the equivalents and illustrating respectively the mono-, di-, and trivalency of sodium, magnesium, and aluminium. The apparatus is fitted up as for a vapour-density determination, with the omission of the outer tube.

Method.

For Sodium.—Use a small weighing bottle or corked test-tube. Quickly cut and dry a small piece of sodium, introduce it into the weighing vessel, and weigh again. This weighed quantity of sodium is allowed to fall down the experimental tube into methylated spirits or a mixture of alcohol and water. The hydrogen is slowly evolved, and is collected in the graduated gas tube.

For Magnesium.—A small piece of bright metal, after weighing, is dropped down the experimental tube into dilute hydrochloric acid. If commercial magnesium be used the amount of carbon in it will introduce an error.

For Aluminium.—Commercial aluminium may be used. A small quantity is weighed out and dropped into strong hydrochloric acid in the experimental tube. Acid in the proportion of ten volumes of acid to one of water is a convenient strength.

* Abstract of a Paper read before the Royal Society, June 3 1903.

Results.				
Weight of metal introduced. Grm.	Volume of hydrogen liberated at 10° C. and 750 m.m. C.c.	Corrected volume. C.c.	Equivalent found.	Standard equivalent.
		<i>Sodium.</i>		
0.078	39.4	37.5	23.21	23
0.074	37.2	35.4	23.32	23
		<i>Magnesium.</i>		
0.0505	48.2	45.88	12.28	12.15
0.0457	43.7	41.66	12.26	12.15
		<i>Aluminium.</i>		
0.0326	42.5	40.46	8.99	9.03
0.0350	45.4	43.22	9.04	9.03

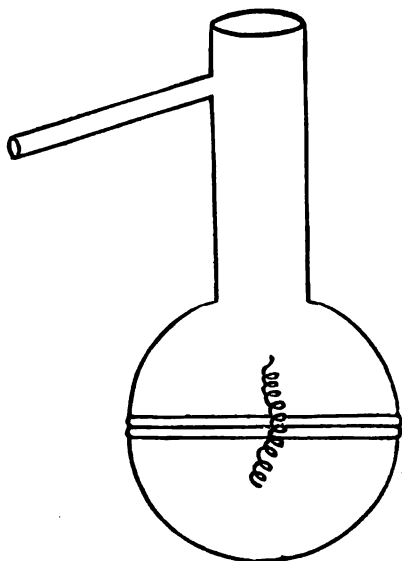
Science Schools, Stroud, Glos.

AN IMPROVED DISTILLATION FLASK.

By JOHN McDONALD.

AFTER the organic chemist has extracted with ether, benzene, &c., he has often to recover the solvent by distillation, and if the substance extracted is a solid it is a matter of some difficulty to get it out of the flask. To overcome this difficulty I have made the following modification.

The flask is made in two parts, which are ground together. The inner edge of bottom half has six small studs of glass projecting up about one-eighth of an inch above the rim, and the upper part just fits over those studs, and has its ground edge fitting on to the ground edge of the under half. The studs are to prevent the two halves from slipping off each other.



The flask is held together by three spiral springs fixed on to three glass hooks placed at equal distance to each other on the upper and under part, and the tension of those springs entirely prevents leaking.

After distilling the two halves are separated by loosening the springs, and the substance can then be conveniently scraped out with a spatula.

The accompanying figure will make the description clear.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.

Introductory.—The term meteoric dust is used because it is commonly applied to the materials forming the subject of this paper; it is not, however, intended to state that the dusts are necessarily wholly of cosmic or extra terrestrial origin. The specimens described and exhibited were from Moruya (fell on Dec. 15th, 1880), from Uralla (fell on Dec. 14th, 1882), from near Broken Hill (fell 1896), from Menindie (fell June 17th, 1899), and Pambula (fell Oct. 5th, 1899). Dust from the roof-beams and mud from a covered cistern at the University, and from the roof of the Observatory, Sydney, were collected in 1882.

All the dusts are of a reddish colour except those from the University and Observatory, which are grey. The red dusts are mainly siliceous and argillaceous, and look as if they had come from dried-up water-holes; they contain a variety of organic and mineral matters such as might be expected from such sources, and in addition magnetite and metallic iron, containing cobalt and nickel.

The University and Observatory dusts also yielded magnetite and metallic iron containing cobalt and nickel.

Meteoric Dust, Moruya, N.S. Wales.—The specimen of meteoric dust forming the subject of this note was forwarded to me by Mr. H. C. Russell, Government Astronomer, who informs me that it fell on December 15th, 1880, at Moruya, a small town in New South Wales, 198 miles south of Sydney and distant 5 miles from the sea.

The specimen consists of a pale clay- or snuff-coloured powder, of uniform tint and appearance; for the most part it is composed of an impalpable dust, but on carefully flattening it out under a spatula and on rubbing it between the finger and thumb a few coarser gritty particles can be felt. To separate the finer material from the coarser particles, a portion of the dust was placed in a tall conical precipitating glass, and subjected to the action of a stream of water carried down by means of a glass tube to the narrow bottom of the glass. The residue left in the glass was found to be made up of grains of quartzose sand and white particles, the latter dissolving readily in dilute acids with effervescence; some of these were grains of amorphous calcium carbonate, but a few of the larger were readily recognised under the microscope as fragments of shells, but whether of fresh-water or marine mollusca could not be decided, as they are much abraded; in addition there are some rather larger soft black particles which readily flatten out under the spatula to an unctuous black mass; when ignited on platinum-foil these black particles slowly burn away with but slight incandescence, like charcoal, but emit a strong empyreumatic odour, and leave a bulky white ash; some of them when crushed and examined under the microscope present a cellular structure very similar to that of wood, but rather obscure; others, however, are devoid of all recognisable structure.

The more or less complete obliteration of the original structure is due to the fact that the wood has undergone considerable change, either by natural decay or by the effects of fire. The woody matter does not, however, present the appearance of ordinary charcoal, such as might have been recently derived from house or bush fires; it has evidently been long subjected to the action of water, and it is highly probable that some of it is not charcoal but simply fragments of water-logged woody matter, black from decay, common in rivers and fresh-water lakes and ponds. Intermixed with the other substances there is also a certain proportion of less decomposed vegetable matter in a flocculent state, and the remains of two or three small beetles were present—all such substances were removed as completely as possible before making the chemical examination; some minute particles of a yellowish mica are

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

scattered through the specimen; mica is common in many muds, especially in those deposited by water running over granite, gneiss, or similar rocks; the rock about Moruya is granite, hence the presence of the mica can be accounted for locally.

As it was thought that particles of metallic iron might be present, a magnet covered with a movable paper cap was repeatedly drawn through the powder, when a few scaly fragments of the metal with jagged edges were obtained—the fragments were found to be malleable, but not highly so, since they rather readily split up under the pestle when crushed in an agate mortar; they also became burnished, and acquire the usual colour and metallic lustre of iron. They at once reduce a solution of sulphate of copper and become coated with metallic copper, apparently just as readily as ordinary iron; they also afford the usual reactions for iron on the application of the wet tests; cobalt is present in sufficient proportion to give the usual blue colour with the borax bead, and I believe that nickel is also present, but the quantity of metal was not sufficient to satisfactorily determine this, neither did it afford conclusive evidence as to the presence of sulphur and phosphorus.

The total quantity of magnetic matter separable by the magnet out of 27.524 grms. of the dust (the whole of that at my disposal) amounted to but 0.009 gm.; the largest fragment weighed 0.0019 gm.

Externally the iron particles are covered with a thin coating of ordinary red rust, the hydrated sesquioxide of iron, and present no traces of fusion nor of the skin of magnetic oxide, usually present on the surface of large masses of meteoric iron.

The minute fused or round globules of iron met with by Mr. Murray (now Sir John Murray, K.C.B.) in the dredgings obtained by H.M.S. Exploring Vessel *Challenger*, were specially sought for, but without success (*Proc. Roy. Soc. Edinburgh*, 1876, 258).

On heating the dust in a glass tube it readily blackens, gives off water with a strongly marked alkaline reaction, and emits an empyreumatic odour; hence there is a notable proportion of nitrogenous organic matter present, and this is confirmed by its behaviour when heated on platinum-foil, for it at once blackens, and the scattered particles of organic matter ignite, and are seen as glowing points or sparks running over its surface; at the same time, a well marked nitrogenous odour is evolved. After burning off the whole of the combustible matter the residue is of a reddish clay-brown colour not materially different from that of the original substance. Apart from the larger woody particles, the organic matter must be very uniformly distributed, since the dust appears on ignition to blacken equally throughout.

Under the microscope the dust is seen to be almost entirely composed of small particles between $1/2000$ th and the $1/500$ th of an inch in diameter, or 0.001 to 0.002 m.m., a few of the coarser grains of sand being about $1/25$ th of an inch, or 1 m.m. Very few of them are quite opaque, the larger grains are colourless and transparent, but most of the smaller particles transmit a yellowish-brown colour; with but very few exceptions the particles are rounded or sub-angular, as if wind or water worn, and with no recognisable traces of igneous fusion. Some diatom frustules are sparingly scattered through the dust; these strongly resemble, and may be identical with, *Diatoma vulgare* and *Savirella constricta*; a few siliceous spicules, something like sponge spicules, are also present; these together with the diatoms are rather more readily detected after treating the dust with nitric acid. A few vegetable fibres, including some filaments of cotton, together with vegetable spores, are also revealed by the microscope. There are also a few scattered minute black non-magnetic particles which are probably chrome-iron, but the quantity is insufficient for me to satisfy myself on this point.

A qualitative examination yielded me the following results:—The presence of organic matter, water both hygroscopic and combined, silica both as free quartz and in combination with bases, mainly with alumina in the

form of clay; iron, metallic, and in combination as oxide, cobalt, and probably nickel, a trace of copper, manganese, lime, magnesia, potash, soda, and small quantities of hydrochloric, sulphuric, phosphoric, and carbonic acids. The dust appears to consist mainly of finely divided clay mixed with other substances.

The hydrochloric acid, as soluble chlorides, is present in rather greater quantity than either the sulphuric or carbonic acids; there is but a trace of phosphoric acid.

An examination with the spectroscope failed to reveal the presence of any rare or unusual element in either the soluble or insoluble portion.

A quantitative examination gave the following results:—

Moisture at 100°	5.400
Loss on ignition	9.700
Silica	58.020
Alumina	17.184
Ferrous oxide	1.214
Ferric oxide	4.237
Lime	2.270
Soda	traces
Potash	trace
Undetermined	1.975

100.000

As the result of the examination, I think that part of the dust is of meteoric origin, but there is also no doubt that the main bulk of it is from terrestrial sources. I do not think it is of volcanic origin, since it does not present the characters of a volcanic ash; there are but few traces of augite or other crystals such as we might reasonably expect to be present in a wind-borne volcanic dust; further the large proportion of combustible matter present is against this idea. Most of it has doubtless been derived from the deposits left by dried-up fresh water pools, lakes, or water-courses, for with the exception of the fragments of shells, the dust is quite unlike a sea-shore deposit; the shells and diatoms may be either of fresh-water or marine origin, the sponge spicules, however, point to the latter source, but these together with other portions of the dust may not have been deposited at the same time. More light would probably be thrown upon the question could specimens of the mud which fell at the same time on board ships off the coast be submitted to an examination.

I do not suppose that much if any of the combustible matter is of meteoric origin, although considerable amounts of carbonaceous and bituminous substances have been met with in several meteorites, e.g., the Bokkeveld, Kaba, and other meteorites; the nickel-iron meteorites found at Bingera, N.S.W., and elsewhere, contain carbon; in fact, carbon is commonly present in metallic meteorites. But I think the metallic portion is of meteoric origin and perhaps part of the earthy matter also. The probability of the metallic portion being of cosmic or meteoric origin is borne out by the peculiar appearance of the iron, its imperfect malleability, resembling in these respects certain other irons of undoubted meteoric origin; by the presence of cobalt and the probable presence of nickel; copper was found in the hydrochloric acid solution of the dust, and it may or may not have been present in the metallic iron also; the quantity of metal extracted by the magnet and separately examined was too minute to determine this. Copper has been detected in many meteorites, and in several specimens of meteoric dust, and it was found, together with metallic iron, cobalt, and nickel, by Mr. J. Y. Buchanan, M.A., F.R.S., chemist and physicist to the *Challenger* expedition, in the clays, manganese nodules, and cosmic dust which were dredged up (*Proc. Roy. Soc.*, 1876, p. 531).

A specimen of dust which fell on board a ship in the Atlantic was found by Gibbs to contain copper; after driving off 18.53 per cent of water the composition was found to be as follows:—

Silica	45.58
Alumina	20.55
Ferric oxide	9.39
Manganic oxide	4.22
Calcic carbonate	11.77
Magnesia	2.21
Potash	3.64
Soda	2.33
Cupric oxide	0.31

100.00 (a)

(a) Watts's "Dictionary of Chemistry," vol. iii., p. 982.

M. G. Tissander (*Comptes Rendus*, lxxxiii., p. 821) states that he found the dust which he collected from one of the towers of Notre Dame in Paris, into which no one had entered for years, to closely resemble that which he detached by friction from meteorites. He found metallic iron, probably of extra-terrestrial origin, in all the samples examined. An analysis of one gave him the following results:—

Dust from the Tower of Notre Dame.

Organic matter rich in carbon	32.265
Soluble in water, chlorides, and sulphates of the alkalis and alkaline earths, ammonium nitrate	9.220
Iron sesquioxide	6.120
Calcium carbonate	15.940
Magnesium carbonate, traces of alumina, phosphates, &c.	2.121
Insoluble in hydrochloric acid	34.344

100.010

In further papers (*Comptes Rendus*, 1876, lxxxiii., pp. 76, 1184) M. Tissander gives additional information upon some specimens of atmospheric dust, and especially upon those which fell on the Canary Islands, February 7th, 1863, at Syracuse, and in Italy on May 10th, 1872, and at Boulogne sur Mer, October 9th, 1876. Drawings are given to show the differences between such meteoric dust and the sands of the English Channel, and of the desert of Sahara. In the same volume, p. 364, there is also a note, by Mr. Phipson, of London, upon the presence of metallic iron in atmospheric dust.

(To be continued).

THE RARE EARTH CRUSADE: WHAT IT PORTENDS, SCIENTIFICALLY AND TECHNICALLY.*

By CHAS. BASKERVILLE, University of North Carolina.

In the movement of economic and social forces the closed century knew four periods of intensified activity. In 1775, a memorable date in American history, Watt began the manufacture of the steam engine. During the adolescence of our own country, revolutions were wrought in the commercial world by the invention of the locomotive by Trevethick (1801), the loom by Jacquard (1801), and Fulton steamed upon the Seine. By the beginning of the nineteenth century, the inventions of Watt and Boulton, Arkwright and Hargreaves, were completed, and something like the modern factory system was begun. From industrial history we gather that "England increased her wealth tenfold, and gained a hundred years' start in front of the nations of Europe."

While vigorous protests, some even violent, as the riots at Lyons and the destruction of Hargreaves' home in England, were made against this rampant spirit of indus-

trialism, there was witnessed a literary renaissance in Great Britain, second only to "the spacious times of great Elizabeth." That age nourished Keats, Shelley, Byron, Scott, Coleridge, Wordsworth, Burns, and Burke. C. Alphonso Smith, in his exquisite essay on "Literature and Industrialism," says: "In a love of nature that made all seasons seem as spring, in devotion to democratic ideals, in variety of range and intensity of feeling, this period takes precedence of Elizabeth's reign." It was of this age that Wordsworth said:

"Joy it was in that dawn to be alive,
But to be young was very heaven."

Granting Tolstoi's definition of science as a "mere gratification of human curiosity," we realise that "science is history making," for it was in this period that Volta and Galvani (1801) gave us a source of power and a means of applying it. At the close of the time, Dalton had announced the atomic theory, and Davy had obtained the alkali and alkaline earth metals.

In the second period, about 1840, there accumulated the potentialities that shaped what is termed the Victorian Era. Quoting Smith again, "In those years, railroads first began to intersect the land, telegraph lines were first stretched, and the ocean was crossed for the first time by steam-propelled vessels. All these mechanical triumphs tended to annihilate time and space. The products of manufacture could now be sent with dispatch to the most distant quarters. Nations came closer together. The two hemispheres became, and have continued, one vast arena of industrial and scientific interchange. . . ."

The literary record of this period contains the names of Tennyson, Goethe, and the Brownings as poets; Dickens, Thackeray, and George Eliot in fiction; Ruskin and Carlyle in miscellaneous literature. In America, during this Mexican war period, we had Longfellow, Lowell, Whittier, Hawthorne, Emerson, and Holmes, "the six names that have given the New England states their incontestable supremacy in American literature."

The part played by the south in literature during these periods was not prominent. The pre-eminence of that part of our country in forensic art and oratory need not be considered, nor need we discuss the social conditions and honest difference of opinion as to the proper interpretation of the true relationship of the government as a whole, and the integral states which constituted it, other than to say that the south, conquered, as was necessary, came out of the Civil War with new economic ideas, with a renewed and "ever-increasing development of her natural resources, with a more flexible industrial system, a more rational attitude towards labour, and more enlightened methods of education, and with it there came a literary and scientific inspiration impossible before." In the year 1870, our third period, which statisticians take as the birth year of the new industrial movement in the south, flashed out new literary stars, such as Sidney Lanier, Charles Egbert Craddock, and George W. Cable. That year can not be named in the presence of scientific men without our thoughts reverting at once to the names of Mendeleeff and Meyer.

The last period is but as yesterday, even to-day.

"All the world's a stage
And all the men and women merely players."

It has been called the age of trusts and mistrusts. In it we must realise that science and its applications must face vested interests; these must be overwhelmed or its universal monopolistic rights be pigeon-holed by purchase. Let us realise, however, in this time, as Boyle has said, that "men often suffer as much cold and wet, and dive as deep to fetch up sponges as to fetch up pearls."

In 1788, Geyer discovered the new mineral, gadolinite, and in 1794, the Finnish chemist, Gadolin, separated a new earth, or oxide, in a black mineral found at Ytterby, near Stockholm, and called it yttria. In 1803, another Scandinavian mineral, then known as "the heavy stone of Bastnäs," or cerite, was discovered by Berzelius and Hisinger and Klaproth in Germany.

* A Lecture delivered before the Chemists' Club, New York, by request, April 8. From *Science*, of May 15, 1903.

In 1839, Mosander discovered lanthanum in this earth. Three years later he resolved it into two elements, one giving a white oxide and the other a pink, namely true lanthanum and didymium. Scheerer noted that yttria, which is white when heated in a closed vessel, becomes yellow when heated exposed to the air. He, in consequence, assumed that it was a complex substance, and the year following (1843), Mosander proved that it could be resolved into three earths, one being colourless (true yttria), the second rose-coloured (terbia), and the third (erbia) giving coloured salts, but a deep yellow peroxide.

H. Rose, in 1839, analysed samarskite and showed it to be a columbo-tantalate of iron and calcium on the one hand, and yttrium and cerium mainly on the other. Satisfactory analyses of this mineral, however, were not had for almost a half-century (Swallow, Allen, and Smith), when its comparatively abundant occurrence was noted in North Carolina.

Shortly after the discovery of the spectroscopic, Gladstone, in 1859, observed the surprising fact that certain substances gave absorption spectra, especially didymium. This constituted the first important, and is now, perhaps, the most valuable criterion in the investigations of many of the rare earths.

In 1860, Berlin, by means of partial decomposition of the fused nitrates, showed the presence of but two earths where Mosander had reported three, namely, yttria, as given above, and a rose-coloured body, which was termed erbia. A reversal of names occurred, for two years later Bahr observed the characteristic absorption spectrum of erbia, and Delafontaine found it in Gadolin's yttria and Mosander's yellow peroxide. The typical oxide was assumed to be RO, and it remained for Mendeleeff in the enunciation of the Periodic Law (1870) to give lanthanum the present accepted formula for its oxide, La_2O_3 .

These elements were obtained as metals—in the then accepted pure form—and Hillebrand and Norton determined the specific heats, which data have aided subsequent workers materially. These determinations, in the light of knowledge gained within recent years, possess a quondam value, however much care and energy may have been expended in securing them.

In 1878, Delafontaine stated that samarskite contained much terbia. He separated a more soluble formate and announced the new element philippium, which Roscoe, although he noted band λ 450, proved to be a mixture of yttrium and terbium. This band in reality belongs to dysprosium, discovered by Lecoq de Boisbaudran. The same year Delafontaine, having found a mare's nest in samarskite, from which Mosander separated erbium, announced decipium. The absorption bands attributed to this element were λ 416 and λ 478, which were subsequently appropriated by samarium, reported as a constituent of didymium by de Boisbaudran. Samarium would now have the name of decipium but for the fact, in 1881, Delafontaine declared his decipia could be resolved into an oxide, without absorption spectrum (true decipia) and one with these lines, or samarium.

J. Lawrence Smith, of Kentucky, in the seventies, announced mosandrum in samarskite. Marignac and Delafontaine independently pointed out that mosandrum was the same as terbium, while later de Boisbaudran demonstrated it was a mixture of terbia and gadolinia. This "nebula of elementary matter," as Petterson puts it in that charming account of the life work of Nilson, appeared to clear up through the work of the English, French, and Swiss chemists, Roscoe, de Boisbaudran, and Marignac. While "the beginning of creation is light," as Carlyle says, the millennium has not yet arrived, for the earths obtained from gadolinite began to break up into a number of new earths.

Cleve (1873) found that the bands of erbium with an atomic weight of 170.5 could be split into those belonging to one element, forming a red oxide with the characteristic emission spectrum (by incandescence) of old erbium and

another group of two absorption bands in the visible spectrum. These were shown to belong to thulium.

Five years later Marignac found all the absorption bands could be eliminated by successive fractioning, whilst the atomic weight of the remaining oxide increased. This oxide gave colourless salts without absorption bands, and the name ytterbium was assigned to it, with an atomic weight of 172.5. In the erbia fractions Soret found bands which could not be attributed to erbium. This body, designated X, subsequently proved to be Clève's holmium.

Material giving out, Marignac, with the true scientific spirit, begged other and younger men to take up the work, using larger amounts. This Nilson did, and verified Marignac's work. Just before reaching the same point Marignac arrived at, however, Nilson obtained a nitrate of a less basic material of lower atomic weight. One fraction continued to drop, while the other rose until, in the year following (1879), assisted by Thalén, who examined the products with the spectroscopic, Nilson separated probably the two best defined of the rare earths, scandium (λ 44.1) and ytterbium (173). Nilson showed the location of these elements in the Mendeleeff table, the properties of the former having been predicted.

Referring to these elements Mendeleeff says:—"These metals, which are rare in nature, resemble each other in many respects, always accompanying each other, are with difficulty isolated from each other, and stand together in the periodic system of the elements." The last statement is based largely upon analogy, a most valuable method of argument in scientific generalisations without doubt, but, as Davy once said:—"Analogy is the fruitful parent of error."

In 1880 Marignac attacked samarskite, and by fractioning the double potassium sulphate obtained two oxides in almost pure state, as follows:—

Y_a giving a white oxide, colourless salts, and no absorption bands. Six years later it was called gadolinium, and the atomic weight 156 assigned it by Marignac, de Boisbaudran, Clève, and Bettendorff.

Y_B proved to be samarium of de Boisbaudran, or Delafontaine's original decipium. Marignac, Clève, Brauner, and Bettendorff determined its atomic weight (149—150). While the elementary character of samarium was questioned by de Boisbaudran and Demarcay as late as 1893, the latter stated that no real proof of the complexity of samarium had been offered. What an exquisite illustration we have here of Tyndall's dictum:—"Every system must be plastic to the extent that the growth of knowledge demands"; for, but a few years have passed before Demarcay (1901) announces europium, with atomic weight of 151 (approximately), obtained by prolonged fractionation of the double magnesium-samarium nitrate. His observations are reported as proved by reversal, absorption, spark, and electric phosphorescent spectra. The element appears to lie between samarium and gadolinium, with several strong lines in the violet and ultra-violet.

(To be continued).

A New Relation between the Electromotive Forces of Saline Solutions.—M. Berthelot.—The electromotive forces developed by the reaction of an acid on a base, and of the corresponding salt on the acid and the base which form it, are connected by a law which the author establishes by a number of experiments performed on six acids and two bases. He further discovers that the law thus established is only a particular case of a more general relation applicable to systems composed of three distinct electrolytes, such as A, B, AB. If E is the electromotive force in a cell containing solutions A and B separated by a porous pot, e_1 the E.M.F. in a cell containing A and AB, and e_2 the E.M.F. in a cell containing B and AB, then the relation $E = e_1 + e_2$ is generally true.—*Comptes Rendus*, cxxvi., No. 23

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 17th, 1903.

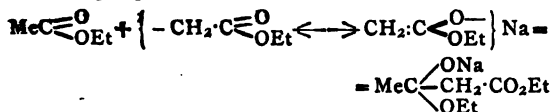
Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 9).

102. "The Acetoacetic Ester Synthesis." By A. C. O. HANN and A. LAPWORTH.

Within the last four years convincing evidence has been accumulated to show that Claisen's hypothesis (*Annalen*, 1897, ccxcvii., 92) as to the mechanism of the synthesis of β -ketonic esters and similar compounds by the use of sodium or sodium ethoxide is incorrect, and, moreover, the facts which led to the formulation of this theory have been shown by Dieckmann (*Ber.*, 1900, xxxiii., 2677) to be capable of a far simpler explanation.

The authors' observations, which are being extended, confirm the view that the acetoacetic ester synthesis is essentially the result of an addition process in which a metallo-organic compound becomes attached to the carbonyl group of an ester—



(compare Michael, *Ber.*, 1900, xxxiii., 3736; and Lapworth, *Trans.*, 1901, lxxix., 1269).

Ethyl bromoacetate was allowed to react with certain esters in presence of zinc and magnesium; with ethyl oxalate, good yields of ethyl oxaloacetate were obtained; with ethyl acetate, the product was mainly ethyl γ -bromoacetoacetate, the latter compound being produced by an exactly similar process, excepting that the reaction occurs between two molecules of ethyl α -bromoacetate without the intervention of ethyl acetate. Fittig, Daimler, and Keller (*Annalen*, 1899, ccxlix., 184) employed this modification of the acetoacetic ester synthesis in preparing diethyl ketipate (diethyl oxalodiacetate), but the complete analogy between the two methods appears to have hitherto escaped notice.

103. "Rimu Resin." By T. H. EASTERFIELD and B. C. ASTON.

Rimu (*Dacrydium cupressinum*; natural order, *Coniferae*) is one of the most valuable of the New Zealand timber trees, the cracks or shakes in the heart-wood being nearly always partially or completely filled by a hard pink resin with a distinctly crystalline fracture.

The chief constituent (75 per cent) of the resin, a crystalline acid, for which the name *rimuic acid* is proposed, melts at 192–193°, distils with very slight decomposition at 296–300° under 21 m.m. pressure, and is optically active. It is easily soluble in alcohol or ether, and dissolves sparingly in water or light petroleum. Its formula, $\text{C}_{16}\text{H}_{20}\text{O}_3$, is supported by analysis, molecular weight determinations, titration values, and analysis of barium, lead, and silver salts. The barium compound is the most characteristic of the salts; it crystallises in well-defined, square plates having the composition $\text{Ba}(\text{C}_{16}\text{H}_{19}\text{O}_3)_2 \cdot 14\text{H}_2\text{O}$. The alkali salts are very soluble and do not separate from solution in the presence of excess of alkali. Rimuic acid is levorotatory, having $[\alpha]_D -159^\circ$ in a 10 per cent alcoholic solution; it yields benzoyl and acetyl derivatives, and its formula may be thus represented: $\text{C}_{15}\text{H}_{18}(\text{OH})\cdot\text{CO}_2\text{H}$. Like most of the acids from the pine resins, it yields no esters when treated with alcohol and hydrochloric acid.

The acid yields two crystalline nitro-derivatives when nitrated in cold glacial acetic acid solution.

104. "Note on the Karaka Fruit." By T. H. EASTERFIELD and B. C. ASTON.

The kernel of the fruit of the Karaka tree (*Corynocarpus*

laevigata; natural order, *Anacardiaceae*), is a staple article of food amongst the Maoris and Morioris. In its raw state it is bitter and very poisonous, but when baked and subsequently soaked in water its toxic properties disappear. Examination of the kernels shows that they contain 15 per cent of a harmless, non-drying oil, and that the aqueous extract of the nut contains mannite, mannose, and dextrose. When the extract is distilled, it yields a considerable quantity of prussic acid. From the aqueous extract, Skey obtained a bitter glucoside, karakin, which, he stated, melted at 100°, and obtained no nitrogen; the authors find, however, that karakin is highly nitrogenous, and when pure melts at 122°. It is most readily obtained from an alcoholic extract of the kernel by removing the alcohol under diminished pressure and re-crystallising the residue from warm water.

Karakin, which has the formula $\text{C}_{15}\text{H}_{24}\text{O}_{15}\text{N}_3$, crystallises in leaflets, and like amygdalin is only slightly toxic when removed from the enzymes with which it is associated. A second glucoside, *Corynocarpin*, can be obtained in small quantity by evaporating the aqueous extract at a temperature below 50° and extracting with ether. As this glucoside cannot be detected in the freshly prepared extract, and as the karakin disappears during the evaporation, it is probable that the second glucoside is a product of the partial hydrolysis of karakin. *Corynocarpin* crystallises in fine needles, melts at 140°, and is less soluble in hot alcohol than karakin.

105. "The Slow Oxidation of Methane at Low Temperatures." II. By W. A. BONE and R. V. WHEELER.

The authors describe an apparatus for the closer investigation of slow combustion processes. This is essentially a closed system in which the reacting gaseous mixture can be circulated day and night continuously, at a uniform rate, (1) over a heated surface the temperature of which is kept constant, and (2) through suitable washing and cooling vessels for the removal of soluble or condensable intermediate products. A specially devised manometer allows of pressure records being taken at regular intervals, so that the velocity of the oxidation may be measured.

Further experiments with this apparatus on the interaction of methane (2 volumes) and oxygen (1 volume) at 450° and 500°, whilst they entirely confirm the authors' previous conclusion that neither hydrogen nor carbon is liberated at any stage of the oxidation, and that the final products consist simply of carbon monoxide, carbon dioxide, and steam, have proved the transient formation of formaldehyde as an intermediate product. In one experiment, 13 per cent, and in another as much as 22 per cent, of the methane burnt was obtained as formaldehyde which had been rapidly removed from the sphere of action by passing the reacting mixture through cold water each time it left the tube containing the heated surface.

The authors conclude that the oxidation of methane involves the following stages:—

1. The simultaneous formation of formaldehyde and steam, by the bimolecular reaction, $\text{CH}_4 + \text{O}_2 = \text{CH}_2\text{O} + \text{H}_2\text{O}$.

2. The further oxidation of this formaldehyde to carbon monoxide, carbon dioxide, and steam. This is probably effected as the result of the simultaneous occurrence of the following reactions:—

a. The bimolecular reaction, $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$.

b. The trimolecular reaction, $2\text{CH}_2\text{O} + \text{O}_2 = 2\text{CO} + \text{H}_2\text{O}$.

106. "The Alkylation of Sugars." By T. PURDIE and J. C. IRVINE.

The method of alkylating hydroxyl groups by means of dry silver oxide and alkyl iodides does not appear directly applicable to aldoses or ketoses, and leads to oxidation and subsequent changes of some complexity; but α -methylglucoside and cane-sugar can be methylated by means of this reaction. α -Methylglucoside, when methylated in methyl-alcoholic solution, yields a mixture of methyl glucose ethers; the main constituent, trimethyl α -methylglucoside, which can be isolated by fractional distillation, is a viscid syrup; it boils at 167–170° under 17 m.m.

pressure, exhibits dextrorotation, and has no action on Fehling's solution.

Complete methylation of trimethyl α -methylglucoside is readily effected with silver oxide in methyl iodide solution, and under these conditions, tetramethyl α -methylglucoside is obtained as a comparatively mobile liquid boiling at $144-145^\circ$ under 17 m.m. pressure; it is dextrorotatory, and has no action on Fehling's solution. Tetramethyl glucose, which is produced by hydrolysing the tetramethylated glucoside with dilute hydrochloric acid, distils without decomposition at $182-185^\circ$ under 20 m.m. pressure, and solidifies slowly, and crystallises from light petroleum in tufts of radiating needles, melting at $81-83^\circ$; it behaves like an aldose, reducing warm Fehling's solution, giving tetramethylgluconic acid on oxidation, and reacting with phenylhydrazine in molecular proportion to form an oil, which is apparently a hydrazone. Tetramethyl glucose is dextrorotatory, but does not exhibit any notable multi-rotation.

The production from α -methylglucoside of a tetramethylgluconic acid, capable of forming a lactone, proves conclusively that the oxygen of the ring in the formula of the alkylglucosides is coupled with the γ -, and not with the β -carbon atom.

A pentomethylated glucose, isomeric with the tetramethyl α -methylglucoside already mentioned, is produced when a solution of tetramethyl glucose in methyl iodide is treated with silver oxide; it boils at $124-127^\circ$ under 8 m.m. pressure, crystallises in slender prisms melting at $42-43^\circ$, and is levorotatory.

Methylfructoside behaves like the corresponding glucoside, and, when completely methylated, yields tetramethyl methylfructoside; the two hydroxyl groups of acetone rhamnoside may also be methylated in a similar manner.

Cane-sugar, on methylation, yields a neutral oil, which has no action on Fehling's solution until it is hydrolysed. The products of hydrolysis are the above-mentioned crystalline tetramethyl glucose and an uncrystallisable syrup, which is probably the corresponding methylated lævulose.

The fact that methylated cane-sugar and methylated methylglucoside give on hydrolysis the same tetramethyl glucose proves that the constitution and linking of the glucose group of the disaccharide is the same as that of the simple glucoside, and affords conclusive evidence, at least so far as the glucose half of the molecule is concerned, of the correctness of Fischer's formula for cane-sugar (*Ber.*, 1893, xxvi., 2404).

107. "Trimethyl α -Methylglucoside and Trimethyl Glucose." By T. PURDIE and R. C. BRIDGETT.

When α -methylglucoside, in methyl-alcoholic solution, is methylated by means of dry silver oxide and methyl iodide, the chief product is trimethyl α -methylglucoside. In preparing this compound, it was found that, in addition to the low methylated derivatives, the tetramethylated glucoside was also produced, but only in small quantity, even when a large excess of the alkylating agent was used. The last hydroxyl group to be methylated undergoes the change more slowly than the others, and it seems therefore probable that the unmethylated hydroxyl of the trimethyl α -methylglucoside is that of the terminal primary carbinol group of the glucoside. The difficulty encountered in completing the methylation is, however, largely due to the loss of alkylating material caused by the production of dimethyl ether. Special experiments showed that the action between silver oxide and methyl iodide is much more rapid in the presence of methyl alcohol, and that the production of dimethyl ether is probably due, not to the direct interaction of the oxide and iodide, but to the methylation of alcohol.

The specific rotation of the trimethyl α -methylglucoside prepared by the authors was much in excess of that exhibited by the specimen referred to in the preceding note. The preparation of tetramethyl α -methylglucoside was also repeated and the substance was found to be more dextrorotatory than the specimens previously examined. The

discordant results may be due to intramolecular rearrangement occurring under the action of methyl iodide, resulting in the production of varying quantities of the corresponding stereoisomeric β -glucosides.

By hydrolysing trimethyl α -methylglucoside with dilute hydrochloric acid, trimethyl glucose was obtained as a viscid, colourless syrup, which distilled without appreciable decomposition at about 194° under 9 m.m. pressure. The substance, which was dextrorotatory and had the properties of an aldose, reduced Fehling's solution in the cold, and ammoniacal silver nitrate on slightly warming; it appeared to react with phenylhydrazine, but the product, which was an oil, could not be made to crystallise. On oxidation with bromine water, it yielded an oil boiling at about 160° under 11 m.m. pressure. The numbers obtained by analysis, and from the estimation of methoxyl, agreed approximately with those required for trimethylgluconic lactone. The lactonic nature of the compound was confirmed by its behaviour on neutralisation, and by the gradual change of optical activity exhibited by its solution.

108. "Note on the Corrosion of an Egyptian Image." By HENRY BASSETT, jun.

An examination has been made of a bronze Egyptian image, about 6 inches high, and having a hollow base filled with lead. This figure probably dates from 200 to 100 B.C., and now bears a mutilated inscription which, according to Prof. Flinders Petrie, reads as follows:—"Khonsu give life to ———, son of ———, born of Saaenhap." It was found in the delta of the Nile, and is very extensively corroded, being covered by a thick, green coating, which in parts entirely replaces the original metal.

The material for analysis was obtained from the base of the figure, and the following analytical results were obtained:—

	Per cent.
Cu	50.65
Pb	6.74
Sn	2.94
Fe	0.15
Ni, Mn, &c.	0.11
Cl	15.71
SiO ₂ (as sand)	1.14
H ₂ O	11.07
(NH ₄)	0.11
	88.62
CuCl ₂	29.34
CuO	46.10
H ₂ O	11.07
SnO ₂	3.73
PbO	7.26
Fe ₂ O ₃	0.22
NiO, &c.	0.14
SiO ₂	1.14
NH ₄ Cl	0.32
	99.32

In the second table, the chlorine has been calculated as copper chloride, whilst the remaining copper and other metals are expressed as oxides.

Traces of calcium were also found, but the amount of sodium present was so small that it could only be detected by the flame test. If all the copper were present in the form of a basic chloride, CuCl₂·3CuO·3H₂O, corresponding with atacamite, this would require 26.84 per cent CuCl₂, 47.57 per cent CuO, and 10.78 per cent H₂O. It will therefore be seen that the substance produced by corrosion is less basic than atacamite. The formation of this mineral during the corrosion of copper and bronze articles when buried in the soil has been shown by Berthelot to be very general (*Comptes Rendus*, 1894, cxviii., 768), but although the formation of this basic copper chloride is in most cases due to the action of the sodium chloride in the soil

(Berthelot, *loc. cit.*), yet in the present instance, ammonium chloride may have played the most important part, since the latter salt was found in amount sufficient for estimation, whereas the former was not.

109. "Contributions to the Chemistry of the Terpenes. Part I. The Oxidation of Pinene with Chromyl Chloride." By G. G. HENDERSON, T. GRAY, and E. SMITH.

When dissolved in carbon disulphide, chromyl chloride and pinene combine to form a solid compound, $C_{10}H_{16}, 2CrO_2Cl_2$, which is decomposed by water, and yields a brown, oily liquid. This liquid, when distilled in steam, yields a quantity of resin and a volatile oil (Etard, *Comptes Rendus*, 1893, cxvii., 434). The authors have found that the oil contains a saturated aldehyde, $C_9H_{15}CHO$, an unsaturated ketone, $C_8H_{14}CO$, and a small quantity of a chlorinated oxidation product of pinene. The aldehyde, which is a crystalline solid with a characteristic odour, melts at $32-33^\circ$ and boils at $205-207^\circ$ (under 755 m.m. pressure); it is insoluble in water, but readily miscible with alcohol and ether. The semicarbazone crystallises in pearly leaflets, and melts at 191° . The aldehyde rapidly undergoes spontaneous oxidation in the air, being converted into a saturated acid, $C_9H_{15}CO_2H$. This acid, which is obtained by oxidising the aldehyde with either boiling dilute nitric acid or aqueous potassium permanganate, crystallises in leaflets or flat prisms, and melts at 117° ; it is only sparingly soluble in cold water, but very readily so in alcohol, and volatilises slowly in steam. The lead salt and the silver salt are obtained as white precipitates; both are soluble in boiling water, but the latter very sparingly.

The ketone is an almost colourless, aromatic liquid, which boils at $206-207^\circ$ under 774 m.m. pressure; its refractive index is 1.4760. The ketone at once decolorises permanganate, and combines additively with 1 mol. of bromine; it yields an oily oxime and a crystalline semicarbazone, which melts and decomposes at $226-228^\circ$; on oxidation with sodium hypobromite, it gives bromoform and *p*-toluic acid.

*110. "Some Physical and Chemical Properties of Strong Nitric Acid." By V. H. VELEY and J. J. MANLEY.

The investigations published by W. N. Hartley in the current number of the *Transactions* (p. 658) on the absorption spectra of nitric acid in various states of concentration, have induced the authors to place on record certain physical and chemical properties of nitric acid varying in concentration from 78 to 100 per cent HNO_3 in continuation of their former work (*Proc. Roy. Soc.*, 1901, lxi., 86, and *Phil. Mag.*, 1902, [6], iii., 118).

Although such properties as density, contraction, refractive indices, and electrical conductivity vary uniformly with percentage concentration from 78 to 92 per cent, yet from this point to 100 per cent there is an exceptional alteration in the variation, reaching a maximum at about 96 per cent, this strength corresponding with an acid which, according to Hartley's view, might be indicated by the formula $3H_2N_2O_6, H_3NO_4$ (=95.9 per cent HNO_3).

Acid having this concentration appears to form a kind of eutectic solution, and therefore presents an analogous, although not strictly parallel case to that of sulphuric acid containing 98 per cent H_2SO_4 , which has been shown by R. Knietzsch (*Ber.*, 1901, xxxiv., 4069) to be a point of critical concentration as regards density, contraction (compare Pickering, *Trans.*, 1890, lvii., 74), electrical conductivity, chemical reactivity, vapour pressure, and, to a less degree, capillarity and viscosity.

As regards chemical properties, certain qualitative experiments have been made on the direct nitration of cotton by nitric acid of approximately 100 per cent concentration without the addition of sulphuric acid.

111. "Notes on Ozone." By J. K. H. INGLIS.

Experiments have been made in order to ascertain the molecular state of ozone when dissolved in acids. In the first place, it was found that the amount of ozone present in an acid solution could be determined by means of the

following reaction: $O_3 + 2HBr = Br_2 + O_2 + H_2O$, the bromine liberated being estimated by potassium iodide and sodium thiosulphate.

In the second place, an investigation of the solubility of ozone in water showed that the solution could not be brought into equilibrium with respect to the gas, since some of the latter was always decomposed on being bubbled through the solution, although the concentration of the latter remained constant. Hence the molecular state cannot be ascertained by means of the solubility relationship.

Lastly, some experiments made on the action of ozone on hydrogen peroxide indicated that these substances acted slowly on one another, manganous sulphate behaving as a catalyser.

Erratum.—Vol. lxxxvii., p. 269, col. 2, line 16 from bottom, for "ammonia," read "methylamine."

PHYSICAL SOCIETY.

Ordinary Meeting, June 26th, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

THE meeting was held, by invitation of Dr. Waller, in the Physiological Laboratory, University of London.

Dr. WALLER gave a demonstration of the Effect of Light on Green Leaves.

The origin of these researches was the result of the consideration of the retinal effects after light stimulation, and the wish to have a sensitive surface naturally spread out for examination. The effect of light is to produce a current (of an E.M.F. of the order of 0.01 volt), at first from the illuminated to the dark parts in the leaf, and later (or as an after-effect) from dark to illuminated. These currents are apparently an index of two opposite processes in the leaf, i.e., dissimilation and assimilation, and give very close analogies to the analogous processes in animal tissues (e.g., Nerves).

Dr. WALLER also demonstrated the "Blaze" currents in Animal and Vegetable Tissues.

These are seen when a strong exciting current (such as an induction-shock of sufficient voltage) is led through a pair of non-polarisable electrodes, and these are then connected with a galvanometer. An electrical response (of greater energy than the exciting current) is given in a direction commonly homodrome to the latter, i.e., in the reverse direction to the ordinary polarisation counter-currents. This "blaze" response is the algebraic sum of post-anodic and post-cathodic currents; the resultant is commonly homodrome, but an anti-drome blaze, distinguished from polarisation by its much greater order of magnitude, is also seen.

Dr. WALLER also showed two methods for the Quantitative Estimation of Chloroform Vapour in Air.

The first was by receiving the mixed gases into a flask of known capacity, absorbing the chloroform by means of olive oil, and reading the reduction of pressure by a manometer. The second was by the simple weighing of a light flask, first filled with air, then filled with mixed air and chloroform vapour. As each litre of the latter is 4.032 grms. heavier than the same bulk of air, by choosing a flask of 250 c.c. each observed milligram of increment is equal to 0.1 per cent of chloroform vapour. Any sized flask can be used, and corrections made for temperature and pressure by the formula:—

$$\log P \text{ per cent} = \log m \text{ (milligrms.)} + \log P \text{ (m.m. Hg.)} \\ - \log T^\circ \text{ (absolute } T^\circ) - \log v \text{ (volume in c.c.)} \\ + 1.8392 \text{ (a constant).}$$

Dr. N. H. ALCOCK exhibited a method of determining the Temperature-limits of Nerve Activity in Warm-blooded and Cold-blooded Animals.

The higher limit was obtained by immersing the isolated nerve in 1.05 per cent NaCl solution. It lies between 40°

C. and 42° C. in the frog, 48° and 49° in the mammal, and is at 53° in the bird, corresponding closely to the coagulating-point of the tissue proteids. The lower limits were obtained by cooling the nerve-chamber as a whole, and taking the temperature of the nerve with a compensated thermo-junction. The limits were -3.5° C. for the frog, $+3.8^{\circ}$ C. for the mammal, $+6.8^{\circ}$ C. for the bird, giving a range of nerve-action of 45° C. to 46° C. for all animals. The method, therefore, permits of an hitherto impossible analysis of actually living nerve-substance.

Prof. AYRTON expressed his interest in the communications, and said he hoped it would be possible to arrange a meeting of the Society at which the points arising from the papers might be discussed.

Two papers by Dr. HARDY, (1) "On the Movement of Unionised Bodies in Solution in an Electric Field," and (2) "On the Passage of Nervous Impulse through the Central Nervous System," were postponed.

NOTICES OF BOOKS.

A Text-book of Organic Chemistry. By WILLIAM A. NOYES. New York: Henry Holt and Co. 1903. Pp. 534.

THE most radical departure from the method of treating this subject as adopted in other text-books is, the author tells us, the dropping of the division into "fatty" and "aromatic" compounds; this arrangement may be justified by the fact that so many connecting links are now known between the two classes of bodies that they no longer stand isolated from each other, but we are afraid that the introduction of the new classification will bring about some confusion in the minds of young students when they hear other chemists speaking of the "fatty" and "aromatic" series of compounds.

The subject of organic chemistry is so vast and is growing so rapidly that few can hope to keep pace with it. This adds to the difficulty of teaching: there is such an accumulation of matter that it becomes difficult to know what to omit and what to insist upon. However, the student will do well to read everything carefully, and to thoroughly master certain portions that will be pointed out to him by his instructor.

The present volume is divided into twenty-five chapters, the earlier ones being on such general subjects as purification, analysis, molecular weights and formulæ, physical properties, &c.; then come the hydrocarbons, all classes of them together, as mentioned above. The oxygen compounds come next, followed by those compounds containing halogens, nitrogen, and sulphur; finally there are three chapters upon heterocyclic compounds, alkaloids, and compounds of physiological and pathological interest.

The index appears to be very full, covering over fourteen pages of two columns each.

CORRESPONDENCE.

RUSTING OF IRON.

To the Editor of the *Chemical News*.

SIR,—An evident error occurs in a letter of mine which you were good enough to print in the *CHEMICAL NEWS* (vol. lxxvii., p. 311).

The formula quoted should be $\text{Fe}_2\text{O}_2(\text{OH})_2$. By a slip of the pen this appears as $\text{FeO}_2(\text{OH})_2$. I should be sorry to seem to attribute so remarkable a composition for rust to Prof. Dunstan.—I am, &c.,

BERTRAM BLOUNT.

76-78, York Street, Westminster,
June 27, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 23, June 8, 1903.

Formation of Alcohol in Fermenting Saccharine Liquids.—Armand Gautier and G. Halphen.—During the process of alcoholic fermentation the ammoniacal nitrogen almost entirely disappears; the basic organic nitrogen increases or remains tolerably constant, whilst the albumenoid ammonia undergoes no sensible variation; the total nitrogen diminishes and the volatile acidity increases all through the process. This acidity, which is always less than 0.1 grm. per litre in grape juice, when it becomes greater than 0.15 grm. per litre, taken in conjunction with the fact of the almost complete disappearance of the ammoniacal nitrogen, constitutes the best method of identifying the fermenting liquor. In grape juice a small proportion of cyclic and non-cyclic organic bases are found which increase in proportion as the fermentation proceeds. Traces of glycerin exist in grape juice, and during regular fermentation these increase in proportion to the alcohol formed.

Action of Arsenic on Copper.—Albert Granger.—Copper combines easily with arsenic when heated in a current of arsenic vapour mixed with an inert gas. A white mass is obtained, which is very brittle and of metallic appearance, and fuses at a red heat. At a temperature of 440° the arsenide of copper, Cu_3As_2 is formed; at a lower temperature, the lower arsenide, Cu_3As .

Qualitative and Quantitative Analysis of Iridium Osmides.—MM. Leidié and Quennessen.—Already inserted.

Hypothesis as to the Nature of Radio-active Bodies.—Filippo Re.—The author believes that the particles constituting the atoms of radio-active bodies have been previously free and that they constitute a nebulous formation of extreme tenuity. These particles in time become re-united round their centres of condensation, giving rise to infinitely small suns, which, by a method of ulterior contraction, take stable and definite forms which make up the atoms of the elements which we know, and which we may compare to small extinct suns. The larger suns which are not yet extinct constitute the atoms of radio-active bodies. The author puts forward various facts in support of this theory.

Curves of Dissociation.—A. Bouzat.—The author's experiments on dissociation curves lead him to the conclusion that, if all the invariant systems in which a solid body dissociates into another solid body and a gaseous body are arranged in the same group, the variation in the entropy which results from the liberation of a molecule of gas under a definite pressure is the same for all the systems of the group.

MISCELLANEOUS.

Physical Society.—A Special General Meeting of the Fellows of the Physical Society will be held at the Royal College of Science, South Kensington, on July 13th, 1903, at 5 p.m., when the subjoined Resolution, which was passed at the Special General Meeting of Fellows held on June 26th, will be submitted for confirmation as a Special Resolution:—"That the Articles of Association contained in the printed document submitted to the Meeting, and, for the purpose of identification, subscribed by the Chairman thereof, be, and the same are hereby approved: and that such Articles of Association be, and they are hereby, adopted as the Articles of Association of the Society."

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th

inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The following were elected members:—Lord Oxmantown, Mr. R. S. B. Hammond Chambers, K.C., Mr. M. B. Field, Mr. H. D. McLaren, Mr. G. Marconi, Mr. R. Pearce, Mr. E. P. S. Roupell, and Mr. W. Wavell. The special thanks of the members were returned to the Misses Gladstone for their present of a portrait of Dr. John Hall Gladstone, F.R.S.

The Allotropism of Tellurium.—D. Bičliankine.—The author has observed that tellurium precipitated from an alkaline solution, and considered by Berthelot to be amorphous, has a density greater than that of the tellurium precipitated from an acid solution by sulphurous acid; these two modifications have not the same appearance. The tellurium precipitated by sulphurous acid is a very finely-divided, black, amorphous powder; the tellurium precipitated by the addition of water and the cooling of a concentrated boiling alkaline solution, is a dark-looking powder containing a number of silvery-looking flakes formed of microscopic rhombohedra. It may be admitted, therefore, that of the three modifications observed by Berthelot, one is amorphous and the other two crystalline. The author found their densities to be as follows:—1. *Amorphous Tellurium Precipitated from an Acid Solution by Sulphurous Acid.*—*d* varied from 5.973 to 6.081; after heating to 430°, *d* varied from 6.036 to 6.201. 2. *Tellurium Fused and Cooled Slowly.*—*d* varied from 6.298 to 6.381; after having been heated to 430°, *d* varied from 6.291 to 6.336. 3. *Tellurium Precipitated from an Alkaline Solution.*—*d* = 6.072 to 6.213; after heating to 430°, *d* = 6.061 to 6.158. 4. *Tellurium Fused and Cooled Rapidly.*—*d* = 6.099 to 6.223.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiii., p. 760.

Influence of the presence of Cerium in Lanthanum containing Didymium and Praseodymium.—R. Marc.—While engaged in the fractionation of didymium by the action of chlorine on the hydrate suspended in an alkaline medium, the author has been led to the following conclusions:—Oxide of didymium is grey in colour when it is perfectly free from cerium, otherwise it is brown. Below 2 per cent, cerium can only be detected in didymium by the colour of the oxide, and no longer by means of peroxide of hydrogen or persulphate of ammonium. The amount of peroxide contained in a brown didymium poor in praseodymium, is proportional to the amount of cerium it contains, provided the latter is not very much. If the proportion of cerium exceeds a certain limit the oxidation extends, not only to the praseodymium, but also to the neodymium; but in the absence of praseodymium, the neodymium is no longer oxidised by cerium. Lanthanum and neodymium prevent the oxidation of praseodymium. In the absence of these two metals the praseodymium is immediately and completely peroxidised by the least trace of cerium; but the smallest quantity of lanthanum or praseodymium retards the oxidation considerably.—*Berichte*, vol. xxxv., p. 2371.

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MICHAELMAS TERM.—Monday, October 5, to Saturday, December 14.

LENT TERM.—Monday, January 4, to Saturday, March 26.

EASTER TERM.—Monday, April 18, to Saturday, July 23.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

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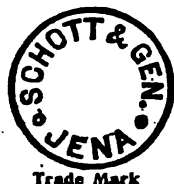
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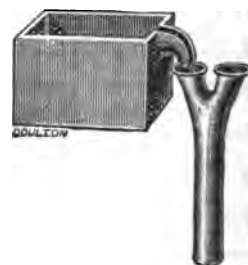
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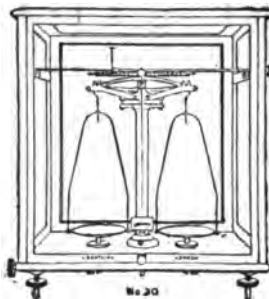
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2277.

NOTE ON THE EFFECT OF EXTREME COLD ON THE EMANATIONS OF RADIIUM.*

By Sir WILLIAM CROOKES, F.R.S.

and
Professor JAMES DEWAR, F.R.S.

As it seemed advisable to examine the action of extreme cold on the action of radium, the following experiments have been made in continuation of work formerly done by either of us separately.

The first endeavour was to ascertain whether the scintillations produced by radium on a sensitive blende screen were affected by cold.

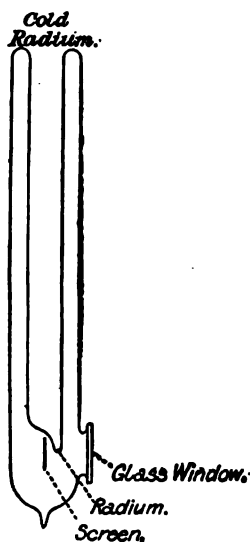


FIG. 1.



FIG. 2.

A small screen of blende with a morsel of radium salt close in front was sealed in a glass tube, and a lens was adjusted in front so that the scintillations could be seen. On dipping the whole into liquid air they grew fainter and soon stopped altogether. Some doubt was felt whether this might not have been caused (1) by the presence of liquid, (2) by the screen losing sensitiveness, or (3) by the radium ceasing to emit the heavy positive ions. To test this two tubes were made, in one of which the radium salt could be cooled without the screen, and in the other the screen could be cooled while the radium salt was at the ordinary temperature. The accompanying sketch explains their construction.

1. Radium salt cooled by liquid air, Fig. 1. Screen at ordinary temperature. Scintillations quite as vigorous as with radium at the ordinary temperature, the screen and radium being *in vacuo*.

2. Radium at the ordinary temperature and screen cooled in liquid air, Fig. 2. As the screen cooled the scintillations became fainter and at last could not be seen. On allowing the temperature to rise the scintillations recommenced.

3. A screen with a speck of radium salt in front of it was sealed in a tube. Water was put in the other end of the tube and the tube sealed on the pump. A good exhaustion

was kept up and the water boiled away, the vapour being condensed in phosphoric anhydride. The tube was sealed off when a few fine drops of water were still remaining in the tube. The scintillations were well seen in this saturated aqueous vapour. The lower end of the tube was dipped in liquid air, which instantly condensed the aqueous vapour and left a very good vacuum. On now examining the scintillations they were if anything brighter and more vigorous than at first. When liquid hydrogen cooling was used instead of liquid air the action was equally marked, showing that the highest vacuum that can be obtained by the action of cold does not diminish the scintillations.

In the upper part of the tube, away from the radium and screen, two platinum wires were sealed to show the state of the vacuum. The spark passed easily at the ordinary temperature, showing a reddish line of aqueous vapour. When the other end of the tube was in liquid air the spark refused to pass.

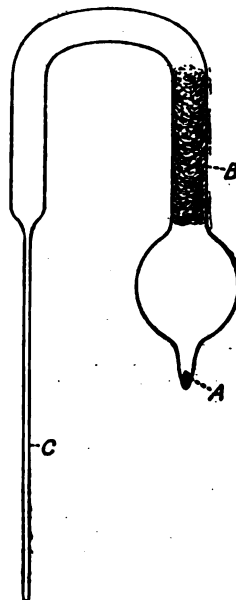


FIG. 3.

4. It was thought that perhaps the passage of the induction spark might have liberated some occluded hydrogen, so another tube similar to the above was made without the platinum wires. Here also immersion in liquid air, if it had any effect, brightened the scintillations, and on replacing the liquid and cooling by liquid hydrogen no change was observable.

In order to test the activity of radium in rendering air electrically conductive, some radium bromide was sealed up in a glass tube and heated to the highest temperature the glass would stand, during the production of as high a vacuum as the mercurial pump would give. The whole tube was then immersed in liquid hydrogen contained in a vacuum vessel. On bringing the radium in such a vessel into a room in which a charged electroscope was placed, it began to leak when the tube of radium surrounded with liquid hydrogen was some 3 feet away, and was very rapid in its action when a foot away from the electrometer. On immersing the tube containing the liquid hydrogen with submerged radium in another large vessel of liquid air and bringing the combination near the electroscope, the action was the same.

The luminosity of the radium salt in liquid hydrogen was much more marked with the pure compound than had been formerly observed with the diluted mixtures containing large quantities of barium salts.

* A Paper read before the Royal Society, May 28, 1903.

Professor Rutherford and Mr. Soddy have made the important discovery that a condensable emanation is diffused into gases from solutions of radium salts, which is capable of condensation from the gas mixture at the temperature of liquid air. As it was important to ascertain what was taking place in this respect with the anhydrous radium bromide when isolated in the highest vacuum, the following experiment was arranged:—

A glass apparatus of the shape represented in Fig. 3 was constructed. The part marked c is a fine capillary drawn out tube some 5 or 6 inches in length, the b portion, about 2 inches long, being filled with hard-pressed purified asbestos. The radium salt was located at A, and the whole was most carefully heated, exhausted to the limit of the mercurial pump, and sealed off. In the dark no trace of phosphorescence could be seen in any part of the apparatus unless from the pieces of the radium bromide. The fine tube c was now immersed in liquid air in a large flask, so that distillation might proceed undisturbed for days. After twenty-four hours of this operation, on looking at the part c while covered with the liquid air, a marked phosphorescence was recognisable owing to some condensed emanation. The luminosity became naturally more marked the longer the time the action was allowed to proceed, and it is our intention to continue the experiments for a lengthened period of time, and then seal off the fine capillary part so that the condensed product may be thoroughly examined.

THE SPECTRA OF NEON, KRYPTON, AND XENON.*

By E. C. C. BALY,
Lecturer on Spectroscopy in University College, London.

THE gases were illuminated by the passage of the discharge from an induction coil through them under reduced pressures. Vacuum tubes were filled with each one of them, and the glowing gas in a capillary portion was examined "end on" through a quartz window. Considerable difficulty was experienced in the use of the vacuum tubes, owing to the rapid absorption of the gas by the electrodes when the electric current was kept passing for long periods. It was found that when the gases were quite pure, and free from any diatomic impurities, the aluminium electrodes were readily volatilised, an aluminium mirror being formed upon the immediately surrounding walls of the tube; at the same time the electrodes became very hot, and it was necessary to make them of very stout wire, e.g., No. 12 B.W.G. Special care had to be taken in making each individual electrode so as to enable it to withstand the disintegrating action of the discharge. The unusual heating of the electrodes gave rise to considerable trouble on account of the large quantities of hydrogen evolved from them; it is a common experience to anyone, when filling a new vacuum tube, to find a quantity of hydrogen given out by the electrodes; this hydrogen, as is well known, may be readily removed by further exhaustion. If, however, into a tube from which this hydrogen has been removed, a small quantity of one of the monatomic gases be introduced, a further large quantity of hydrogen is evolved from the electrodes. Every trace of this second quantity of hydrogen must be removed before the tube can be depended upon; it is necessary to thoroughly wash out the tube by repeated admission of argon and re-exhaustion.

The measurements were all made upon photographs taken with a Rowland concave grating of 10-foot radius and 14,438 lines to the inch; the first three orders of spectra were employed, and nearly all the chief lines were measured in two orders. As far as can be estimated by the coincidences between the different spectra, the probable error is less than ± 0.003 Angström unit. The spectra are

all composed of bright lines and are absolutely characteristic in each case. While neon possesses only one spectrum, krypton and xenon both have two, one being given when the ordinary discharge is passed and the other when a Leyden jar and spark gap are placed in the circuit; this second spectrum is much more complex than the first in each case, an analogy being thus shown with argon.

There are about forty lines of weak intensity common to the jar and spark gap spectra of krypton and xenon; this may possibly be considered as evidence of the existence of another element of higher atomic weight in the same series.

In the tables of the spectra, columns are given of the measurements which have appeared by Liveing and Dewar and by Runge in the case of krypton. A very satisfactory agreement is to be observed between the two series of measurements, although those of Liveing and Dewar are only given to the fourth place. It is interesting that these authors give, in their list of the spectrum lines of the most volatile gases of the atmosphere, about 162 lines which do not appear on the neon photographs, and, therefore, in all probability, do not belong to this gas.

The most important lines in the visible region of the spectrum are given in the following tables:—

Wave-lengths. Intensity. Wave-lengths. Intensity.

Neon Spectrum.

6402.40	10	6096.37	10
6383.15	8	6074.52	10
6328.38	6	6030.20	10
6304.99	8	5975.78	8
6266.66	10	5974.73	6
6217.50	8	5944.91	10
6182.37	10	5882.04	8
6163.79	10	5852.65	20
6143.28	10	5764.54	8
6128.63	8	4259.53	6

The First Krypton Spectrum.

5871.12	10	4454.12	10
5570.50*	10	4400.11	6
5562.45	6	4376.33	10
4671.40	10	4362.83	9
4624.48	10	4319.76	10
4502.56	9	4318.74	8
4501.13	7	4274.15	10
4463.88	10		

* Probably the green Aurora line.

The Second Krypton Spectrum.

5633.17	6	4109.38	6
4765.90	6	4098.89	7
4762.60	5	4088.48	8
4739.16	7	4067.53	5
4659.04	5	4065.22	8
4634.05	5	4057.17	8
4619.31	6	4050.62	5
4615.46	5	4044.80	5
4577.40	6	3998.10	5
4523.32	5	3994.98	6
4475.18	7	3954.90	5
4355.67	10	3920.29	8
4317.98	5	3917.76	6
4300.67	5	3912.69	5
4293.10	6	3906.37	8
4145.28	6		

The First Xenon Spectrum.

4923.28	6	4524.83	6
4916.63	6	4501.13	10
4807.19	6	4193.70	8
4734.30	8	4116.25	7
4697.17	7	4109.84	5
4671.42	10	4078.94	10
4624.46	15	3967.74	10
4582.89	5	3951.16	10

* Abstract of a Paper read before the Royal Society, June 18, 1903.

The Second Xenon Spectrum.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
6097.80	7	4603.21	10
6051.36	7	4592.22	6
6036.40	6	4585.65	10
5976.67	7	4577.36	6
5751.28	5	4545.34	8
5727.15	5	4541.03	8
5719.83	6	4532.67	5
5667.85	6	4524.38	5
5659.67	5	4481.01	7
5616.99	6	4462.38	20
5531.33	7	4448.28	10
5472.90	7	4434.35	6
5460.63	6	4415.00	7
5450.71	5	4406.99	5
5439.19	8	4395.91	10
5419.40	10	4393.34	10
5372.62	8	4330.63	15
5339.56	9	4296.52	5
5314.15	8	4245.54	10
5292.40	10	4238.37	10
5262.16	5	4223.14	5
5260.65	5	4215.77	5
5191.60	5	4214.17	5
5080.88	7	4213.80	5
4921.68	6	4208.61	6
4890.24	5	4193.25	8
4887.47	5	4180.20	10
4883.68	6	4158.14	5
4876.68	7	4145.85	5
4862.69	8	4109.20	6
4844.50	10	4057.55	5
4823.47	6	4050.19	6
4698.20	5	3992.98	5
4683.76	5	3950.70	8
4652.15	6	3922.67	10
4615.72	5	3908.00	7

The total numbers of lines measured in the five spectra are as follows:—

Neon	164 lines
Krypton I.	74 "
Krypton II.	700 "
Xenon I.	92 "
Xenon II.	1370 "

There, 17 lines which are common to the two Krypton Spectra, and 7 common to those of Xenon.

THE RARE EARTH CRUSADE: WHAT IT PORTENDS, SCIENTIFICALLY AND TECHNICALLY.*

By CHAS. BASKERVILLE, University of North Carolina.

(Concluded from p. 19).

In 1883 Crookes brought into consideration phosphorescent spectra obtained in a vacuum tube under the influence of an electric discharge. The year following, Lecoq de Boisbaudran obtained another method of securing a phosphorescent spectrum. It is, in fact, an inverse spectrum, nearly related to that of Crookes, very delicate, being greatly influenced by small amounts of foreign bodies and other conditions. The brilliancy of the bands thus obtained does not depend upon the proportion of the active substance present. A small amount of the body with much inert material gives a bright spectrum, consequently it offered little promise as a method for following the process of fractionation.

Up to this time holmia and thulia had not been freed

* A Lecture delivered before the Chemists' Club, New York, by request, April 8. From *Science*, of May 15, 1903.

from the other earths. In 1886, de Boisbaudran showed that holmia was composed of true holmium (162) and dysprosium (?), adverted to, characterised by several bands, the one to which Sir William Crookes called especial attention being λ 451.5. This Englishman later (1889) subjected yttrium salts to a great number of fractionations, several thousand, finding the bands of the original material distributed among the different fractions. From this work he assumed that yttrium could be split into a number of elementary substances, which he termed "meta-elements," naming one victorium after the lamented Queen. Without doubt Sir William Crookes enunciated in this paper an important principle in inorganic research, namely, what may be termed "partial cleavage"; that is, the fractioning of a complex mixture of elements may be pushed to an extreme with one compound, and the bodies appear elementary. On applying another method, or the same method to another compound, of the assumed elementary substance, the cleavage may be brought about in another direction, and so on. The "genesis of the elements" was the natural theory offered by that mastermind. It was strongly combated in the main, however, by de Boisbaudran, who showed that two of the bands obtained, $Z\alpha$ and $Z\beta$, are not at all related to yttria, as the former follows holmium and the latter is identical with terbium. He says, further:—"Perfectly pure yttria gives no phosphorescent spectrum." Dennis, the American worker on the element in question, appears to agree with the French chemist.

It may be recalled that Delafontaine extracted samarium (his original decipium) from Mosander's didymium. The theoretical work referred to naturally gave rise to the complexity of didymium, which has an absorption spectrum characterised by a number of well-defined bands. In fact, Clève made the prediction of the presence of another element in lanthanum and didymium in 1878. Carl Auer (von Welsbach), in 1885, by prolonged fractional crystallisation of the double ammonium nitrate, obtained from the pink solution green salts of praseodidymium (140), and rose-red salts of neodidymium (143). The absorption spectra of these two are complementary. The next year, Crookes eliminated band after band of the didymium until only λ 443 remained. Krüss and Nilson, and Kieserwetter and Krüss, prepared didymium from several sources, fractioned the preparations, and arrived at a similar conclusion. It is now known, as shown above, that erbium has been resolved into seven other well-characterised elements, viz., besides erbium (166.3), scandium (44.1), yttrium (89), terbium (160), ytterbium (173), thulium (170.7), holmium (162), and dysprosium (?). After the elimination of samarium, didymium shows at least nine distinct absorption bands:— λ 728.3, 679.4, 579.2 to 575.4 (which is easily resolved into two), 521.5, 512.2, 482, 469, 445.1, and 444.7 (443) (ultra-violet and infra-red not considered). In short, these two elements, neo- and praseodidymium, consist of at least nine elements. The full conclusion of Krüss and Nilson may be stated in their own words:—"Nach obigen Auseinandersetzungen hätten wir an Stelle des Erbiums, Holmiums, Thuliums, Didyms, und Samariums die Existenz von mehr als zwanzig Elementen anzunehmen."

While the acceptance of such conclusions without question would be wholly unscientific, we must carefully consider the general idea involved, and the investigations upon which the conclusions were founded, and the investigations carried out subsequently to test them. Absorption bands determined under variable conditions are not to be accepted as essential characteristics of new elementary substances, as they have been shown to vary with the salts used. Sorby and Liveing have shown that the character of the solvents and traces of impurities bear importantly upon the intensity of the absorption bands. Lawrence Smith and de Boisbaudran, and latterly Dennis and Chamot, have called attention to variations in the absorption spectrum of didymium, when nitric acid is present. Becquerel showed there were variations in the spectra of

crystalline compounds of the same element. Very recently Muthmann and Stützel have shown that if a substance be regarded undecomposable, its absorption spectrum varies considerably with dilution and amount of free acid present. Demarçay has urged the necessity of giving the thickness of the medium used, with a statement of its strength.

C. M. Thompson reported that didymium salts from various sources showed no material differences in absorption spectra. Schottländer remarks, however, that the material used contained several oxides, giving absorption bands, so the intensity of certain bands of a particular element may have been increased by the superposition of bands of other elements.

Crookes and Dennis independently made the extremely interesting observation that the heavy orange bands (575—579), which were resolved by Auer, were not altered in their fractions when the remaining lines had undergone some changes, hence the former stated that probably "didymium will be found to split up in more than one direction, according to the method adopted." The work of Dennis on the relative intensities of the bands observed, by varying the procedure of fractionation, is in direct accord with the observations of previous investigators as to the compound nature of neo- and praseodidymium.

Von Scheele (1898) carried out a series of investigations looking toward the proof of the elementary character of praseodidymium. Bettendorff, by a spectroscopic examination of the mother-liquors obtained by the Welsbach method, confirmed the observations of Krüss and Nilson, especially with regard to the absorption bands in the blue portion of the spectrum. Schottländer working with the same object in view, came by no means to the same conclusion. He held it probable that praseodidymium consists of a mixture of two elements, whose oxides burned in air give R_2O_3 and RO_2 (i.e., $R_2O_3 + 2RO_2 = R_4O_7$, the accepted peroxide). His conclusion was founded upon the small per cent of oxygen present in the peroxide. Forshing confirmed Bettendorff's results spectroscopically, and reported $Pr \alpha$ characterised by the yellow bands, and $Pr \beta$, which has the three bands in the blue, indigo, and violet. Boudouard arrived at the same conclusions. Brauner concluded, in his work on the oxides, "from the tendency of them both (praseodidymium and neodidymium) to become more highly oxidised than would correspond to the formulæ Pr_2O_4 and Nd_2O_5 , that praseodidymium and neodidymium may be further split up."

Von Scheele maintains that none of the savants has proved Krüss and Nilson's theory that there are four elements present in praseodidymium. By long repetition of the Welsbach process he failed to bring about any variation in the yellow bands, which Bettendorff maintained could be fractionated away, and demonstrated to his own satisfaction the elementary composition of praseodidymium in a paper reciting much careful and patient experimentation. Unfortunately, he ignored the work of Crookes and Dennis, which is dependent upon variation of the finer details of manipulation. In our laboratory, following entirely novel lines of research for this element, we have apparently verified the conclusion of the complexity of the element in question.

The material used was generously presented by Mr. H. S. Miner, the long-time associate and successor of the lamented Shapleigh. It was quite free from neodidymium, but contained a notable amount of lanthanum. The presence of lanthanum facilitates the fractioning of didymium by the Auer method, as pointed out by Dennis. A pure praseodidymium compound is readily had by using the method of Baskerville and Turrentine, namely, fractioning a citric acid solution saturated with the hydroxide, and heating. The citrate obtained was converted into the oxide. This oxide was free from the other elements giving absorption bands in the visible spectrum. So far we have not been able to examine the ultra-violet, but shortly expect the arrival of one of Wood's nitrosodimethylaniline screens, which I am having made for my spectroscope. The instrument is a Steinheil plane grating (made by

Brashear) with 14,438 lines to the inch, essentially the same as that described by Dennis in his work with Dales on yttrium, except a size larger. It was purchased by a grant from the Bache Fund of the National Academy. The oxide was proved to be free from elements which give no absorption band, especially lanthanum, by means of photographs of the arc spectrum obtained with a Rowland concave grating (15,000 lines to the inch and twenty-one-foot diameter). The spectrograph work was done by my friend Dr. W. J. Humphreys, of the Department of Physics, University of Virginia, and will be published by us in full at the proper time. The oxide was very carefully treated with hydrochloric acid, bringing about partial solution, whereby a distinct brown oxide was obtained different from the normal black peroxide; further, a separation has been secured by fusion with sodium peroxide.

Other methods of attack have been followed, as, for example, fractional crystallisation from a concentrated chloride solution by means of gaseous hydrogen chloride, fusing with alkaline hydroxides, sodium dioxide, &c. The details will be given in the full papers when published.* Suffice it to say that we have succeeded in obtaining a preparation which has lost entirely the absorption line λ 443, and another, very small in amount, which shows only that line. The oxide is bright green when heated in the air. The work of Crookes and Dennis is thus verified by entirely novel methods. Drossbach reports the existence of an element in monazite sand with an atomic weight of 100; that is, eka-manganese, but it is discredited by Urbain.

It may be interesting at this point to call the attention of the scientific men of America to the fact that from the locality, Ytterby, where cerite was found, four elements, yttrium, erbium, terbium, and ytterbium, have secured a name. From the occurrence of samarskite and monazite (Mitchell and McDowell, and other counties in North Carolina and Brazil), which contain most of these rare earths, and have furnished so much of the material for the researches, not a single element is named, except the tentative carolinium, which will now receive attention.

The other rare earths to which I wish to direct your indulgent attention in a few words are those which possess radio-activity, a property accidentally re-discovered by Becquerel. It may be remarked that Sir George Stokes fifty years ago addressed the physicists of the British Association on the curious action of certain bodies in emitting light at ordinary temperatures. Little was then known of the phenomenon of fluorescence. There is not time to attempt a discussion of the origin and nature of radio-activity. It appears that our satisfactory Maxwellian theory of the progression of ethereal stresses may yet be harmonised with the older corpuscular view of Descartes and Newton by the recent elegant researches of Becquerel, J. J. Thomson, Rutherford, Giesel, and others.

M. and Mme. Curie have been pioneers in utilising this physical activity, which serves to detect the presence of minute amounts of certain elements contaminating hitherto well-defined bodies. J. J. Thomson, in his recent extremely interesting address at Belfast, brings out a point demanding the chemist's closest attention, namely, that the radio-activity is five thousand times as delicate as the spectroscopy, it matters not whether the arc, spark, absorption, or phosphorescent spectrum be made use of.

By prolonged fractionation the Curies separated radium from barium salts. Demarçay has prepared the spectrograph showing the characteristic lines of the element, while Mme. Curie determined its atomic weight (225). It fits beautifully in Mendeleeff's table. The Curies have also announced polonium, or the active constituent of bismuth. Uranium appears to have been the first to show this property, as noted by Becquerel. Actinium, it seems, is the

* I have been assisted in the numerous researches, barely summarised in this address, by Messrs. J. E. Mills, R. O. E. Davis, J. W. Turrentine, James Thorpe, Reston Stevenson, W. O. Heard, Hazel Holland, E. B. Moss, H. H. Bennett, Geo. F. Catell, and F. H. Lemly. The separate papers will shortly be published. Three grants of fifty dollars each have been made by the American Association for the Advancement of Science to aid in the work on the rare earths.

elusive body found in pitchblende by Curie, and appears to be the same as Crookes's uranium X.

Chroustschoff a dozen years ago announced that thorium contained another element, which he called russium. I have been unable to secure a copy of this paper or even to learn where it appeared. I am informed by Prof. Mendeleeff, who mentions it in his "Principles of Chemistry," that Chroustschoff made the announcement before the Russian Chemical Society, but had published no complete investigation. Two years ago, Brauner, working along one line, and I, on another, independently announced the complexity of that element.

It is generally accepted now from the published work that the property of emitting rays which affect the photographic plate is not a specific property of thorium, but characteristic of a constant contaminating constituent of that element. It is well known also that, while some of these radiations or emanations affect the photographic plate, some do not. The electrical method of measurement (quantitative) has been substituted in our work, and improved methods of fractionation are being used, whereby we seem to be approaching a non-radio-active thorium and one possessing that property in high degree. Further, similar compounds of thorium fractions similarly treated show almost no difference with the Rowland grating referred to, yet show marked divergence in their radio-active properties. The radio-active work is being done by Mr. G. B. Pegram, of the Department of Physics in Columbia University.

I have not come from "away down south" to the centre of commercial activity of all the Americas to tell you how these rare substances are to be had at low cost, advertise their uses, form a combination, and arrange for their sale at a good profit, although one of my neighbours ranks high among Knickerbocker mergers. The fourth period in rare earth activity is co-existent with the extension of the use of some of them for illuminating purposes. The price of thorium nitrate fifteen years ago was over five hundred dollars per pound. Now the market price is about five dollars per pound. Commerce required thorium compounds; they were provided. Commerce demanded thorium compounds at a reasonable price; the demands were met. The prices of certain of the impure rare earths occurring in nature with thorium are high, but their values do not follow well-known economic laws, and are purely fictitious. When uses are found, the prices of these by-products will fit the demand.

In this maze of an enticing problem one imagines much, and many speculate more. Not unfrequently, especially of late, have we been treated with irenic disquisitions as to the location of these rare elements in the natural system. It appears to be forgotten that Mendeleeff used his table to correct the formulæ of the typical oxides of certain elements, as, for example, lanthanum (LaO to La_2O_3). The fact is forgotten that the atomic weights now ascribed would be materially different were the type different. The ascribed atomic weights are dependent upon the synthesis or analysis of the sulphates almost without exception. It is forgotten that "-yl" salts, like uranyl, chromyl sulphates, are possible for these elements, as recently shown by Blandel for titanium and Matignon for praseodymium and neodidymium. Furthermore, it is forgotten that the sulphate method is absolutely defective, as Schützenberger pointed out. This has been verified by Wyruboff, Dennis, Brauner and Pavlicek, and Damarçay, as well as myself. Therefore, all attempts to arrange these elements, some of which are known to be complex, in the periodic table are veriest speculation, which can profit little. It is quite as true also that the table should receive no discredit because it fails to account for them with our present knowledge. According to its author the table reserves twenty-three places for their occupancy.

Two desiderata may be mentioned:—1. Satisfactory tests, preferably colorimetric, which may be quickly applied, as Hillebrand has remarked about titanium. This supplied, perhaps these earths would not be so rare. I

have shown the universal occurrence of titanium. 2. Spectral data from more highly purified substances, for much that is now at hand has been obtained from impure earths.

The methods of attack at present are mainly based upon the same phenomena of oxidation, reduction, and saturation. The applications are different, however. As typical examples, a few may be cited as follows:—Melikow has been using the hypochlorites, virtually the Lawrence Smith method; Muthmann, hydrogen dioxide and acetate solutions; Dennis is using organic acids, as did Metzger for thorium; Jefferson and Allen have applied certain organic bases for analytical purposes, while in our laboratory we have saturated the stable alkalis, fused with sodium peroxide, and reduced with such basic reducing agents as hydrazine and phenylhydrazine, and so forth.

All is not dark, for rifts in the clouds are making. Old Watt said:—"Nature has always a weak side, if we can only find it out." Looking back and with that century of experiences we can frequently in a measure judge of the future, and those things which make toward the true end.

Naturally a sequel is due this paper, and I look forward to presenting it in my Vice-Presidential Address before Section C of the American Association at the St. Louis meeting. Some sequels are better than their predecessors; Most of them, however, are not so good.

ON THE RADIO-ACTIVE EMANATION IN THE ATMOSPHERIC AIR.*

By J. ELSTER and H. GEITEL.

I.

ON THE ORIGIN OF THE RADIO-ACTIVE EMANATION CONTAINED IN THE AIR OF THE GROUND.

By H. GEITEL.

ONE of the objects to which we have directed our attention since the last conference at Göttingen has been the elucidation of the abnormal amount of radio-active emanation contained in the air of cellars and caves, with which its high ionisation is very closely connected. This might conceivably be due either to an as yet unknown power of stagnant air of giving rise to such emanation spontaneously, and of storing it up in itself, or to a diffusion of the latter from the surrounding walls and from the soil. Many facts may apparently be brought forward in favour of the first assumption of a self-activity, namely the actual spontaneous rise of the conductivity of hermetically sealed quantities of air, and the failure of all efforts to discover a trace of primary radio-activity in the material of the walls of cellars and caves.

Experiments with a greater quantity of air, which was shut up for some weeks in a boiler, showed, however, that no appreciable accumulation whatever of radio-active emanation occurred during this time.

So there only remained the assumption that the walls of the subterranean spaces, or the air diffusing from the surrounding earth through their pores, were the carriers of the emanation. It was, in fact, afterwards proved that the air removed by simple suction from the soil at our dwelling place was charged with active emanation, and that its activity actually exceeded that of the air of cellars and caves. (We have already published these results in *Physikal. Zeitschrift*, 1902, iii., p. 574). By the investigations of Ebert and Ewers, this property has been demonstrated in the case of the air from the ground of Munich also (H. Ebert and P. Ewers, *Physikal. Zeitschrift*, 1902, iv., p. 162).

How far the nature of the soil at the place of observation influences the activity of the air contained in it was then the next point to be examined.

* Aus der Denkschrift der Kommission für luftelektrische Forschungen, München, 1903.

Here also two different assumptions might be made. Either that activity was a universal property of the air of the ground independent of the nature of the soil, or it was the result of a certain amount of primarily active substance contained in the material of the soil itself. While, in the first case, samples of air of any origin (so long as they undoubtedly consisted of the air of the ground) must show equal activity, in the second case, an inequality of the activity was to be expected, as it could hardly be supposed that the inducing active substance would be present in the soil with the same activity in all places.

Some results obtained previously pointed to the last alternative.

Thus the conductivity of the air in cellars and caves, measured by means of the leakage apparatus, showed in different places considerable differences, which could only be explained as being due to the influence of the containing walls. Thus we found high ionisation of the air in the cellars of our dwelling place (about six times the normal), and in the Baumanns and Iberg caves, in the Hartz (nine and three times the normal),* but a considerably smaller ionisation in cellars in Clausthal, in the Hartz, and in Zinnowitz, on the Baltic Sea (from 1.3 times to twice the normal). In a large space in a potassium chloride mine at Vienenburg, in the Hartz, the ionisation of the air was actually less than in the free atmosphere, but here the conditions were certainly unfavourable, as the air contained distinct traces of the fumes of the blasting materials.

In connection with this, an experiment at Clausthal, in the Hartz, was, however, specially instructive. An insulated copper wire, negatively charged by means of an influence machine, was held for an hour in free air, and another in a cellar; the activity excited was, in the case of the first, eleven times greater than in the case of the latter. Thus here the free air actually contained more active emanation than that of the cellar, a condition of things which is completely contradicted by previous experience.†

Hence it was most probable that samples of the air of the ground of different origin would have different activity. In order to obtain more definite grounds for this opinion, it was necessary to find a method of removing the air from the ground of different places, and of comparing the activity of these samples. As it is not generally practicable to perform the test for radio-activity on the spot, the samples must be securely sealed in easily transportable vessels. The time necessary for removal to the place of examination, as long as it only amounts to a few hours, is without appreciable effect on the result; an interval of two or three days was even allowed for longer distances, when it was only a question of confirming results by rough experiments. If a longer time elapses between filling the transport vessel with the sample of air and examining the latter, the activity is found to have become too small, and after about four weeks it had disappeared in a sample obtained from Wolfenbüttel. For the removal of the air from the ground, an egg-shaped vessel of three litres capacity was employed; it could be closed at both ends by means of well-fitting cocks. Before being used it was filled with water, and held vertically with both cocks shut. The upper opening was connected, by means of rubber tubing, with a measuring tube about 1 m. long; this was driven into the soil until only a few c.m. projected. When the cocks were cautiously opened, the water flowed out through the lower, while the air from the ground passed in through the upper. When the vessel was completely filled with the air, both cocks were hermetically closed.

To perform the investigation, we allowed the air to pass through water into a bell-glass of about 30 litres capacity; beneath the bell-glass was placed a leakage apparatus, without the protecting cover (Cf., *Physikal. Zeitschrift*,

loc. cit.), surrounded by wire gauze. The quantity of electricity escaping in a given time served as a standard for the ionisation of the air which was introduced into the bell-glass. Before every experiment the bell-jar was filled with the air of the room, and the loss of electricity was determined before the admission of the air of the ground, and also at the end of each series the loss in the case of the electroscope. This last was always so small that it could be neglected throughout, since the whole method employed was somewhat inaccurate.

With the potential of 100 to 200 volts employed, the saturation current beneath the bell could be regarded as reached. The fall of potential in 15' in ordinary air, the mean value of which amounted to 14 volts, is henceforward adopted as unit for the ionisation of the air beneath the bell after the introduction of the sample to be examined. This ionisation can also be taken as a standard for the amount of radio-active emanation.

By the method thus described, we have examined samples of air from different places. Those which were obtained from the clayey and limestone soils of the gardens in Wolfenbüttel were strongly active, though not all equally (activity on the given scale lay between 16 and 4). A sample taken from a gravel pit in the neighbouring wood was decidedly less active (activity = 3). The air from the ground at Wolfenbüttel had the same activity as a sample from Göttingen (activity = 12). A sample from the clay slate of Blankenburg-a-H. was much less active (activity = 2.3); the activities of the air from the shell limestone of Würzburg,* and from the basalt of Wilhelmshöhe, near Kassel, were still smaller (activity = 1.6 and 1.01 respectively). These results were sufficient to show that the nature of the soil from which the air was drawn must have a considerable influence on its activity, and the next thing to do was to seek for a primary radio-activity of its constituents.

As has already been mentioned, our earlier attempts as well as those of Ebert and Ruf (*These Sitzungsprotokolle*, May, 1902; also *Physikal. Zeitschrift*, 1902, iv., p. 93), to prove the existence of a primary Becquerel radiation in the materials of the walls of cellars and caves, were certainly unsuccessful, but in these experiments, only the building materials and the solid rock were examined, and not the loose soil itself. We now filled a zinc dish, of diameter 29 c.m., and height 2.5 c.m., with earth which had been dug up from some centimetres below the surface of the garden of our house, and introduced it under the bell-glass described, in such a manner that the electroscope rested with the enveloping wire gauze on this earth.

Immediately an undoubted increase in the ionisation of the air beneath the bell became apparent, as must be expected in the presence of a feebly radio-active substance; in the course of from two to three days this rose to a maximum value of about three times the normal. It did not matter in this experiment whether the earth was in the moist condition in which it was removed, or whether it was introduced underneath the bell-glass after protracted drying; after the lapse of eight months no decrease of activity was apparent in the material used for the first experiments. The soil from the field and from gardens situated outside the town behaved in the same way as that from our garden, and a grayish blue clay from a pit in the neighbourhood was also active; but, on the other hand, a white quartz sand (containing limestone) was inactive.

The next thing to do was to make an attempt to separate off the inactive substances of the soil by chemical means, and thus concentrate the activity in smaller masses. The clay, which formed a homogeneous mass after washing away the coarser lumps in it, seemed to be most suitable for this purpose. By extraction with dilute hydrochloric acid all the calcium carbonate present could be completely removed, and the residue, after drying, immediately showed a lower activity than before the treatment; but this increased in a few days (during which the substance was

* Dr. Cuomo, of Capri, kindly informed us that he has observed also abnormally high leakages (about three times the normal) in some stalactite caves there.

† We take this opportunity of heartily thanking Prof. Gerland, of Clausthal, who rendered this experiment possible.

* Our thanks are due to Dr. Harms, of Würzburg, for sending us samples of air from that place, and from Göttingen.

kept outside the bell-glass) to about the original amount. Again digesting with hydrochloric acid, or dilute sulphuric acid, at first caused a decrease of the activity, but this also was restored in course of time. Unfortunately, on account of the great quantities of the substance to be treated, it was not possible for us to evaporate to dryness the liquid which had been in contact with the clay quickly enough to examine the residue for radio-activity, but from the behaviour here described, there seemed to us to be no room for doubt that an active substance was present in the clay which we examined; this, like thorium oxide, according to Rutherford and Soddy's researches (E. Rutherford and F. Soddy, *Phil. Mag.*, 1902, p. 370), forms a more strongly active substance soluble in acids (comparable with Rutherford's ThX) which after extraction with acids is gradually regenerated. The same phenomenon as in the case of clay we found also in the so-called cave loam (Loess) from the Baumanns caves in the Hartz.

In order to have better defined substances to deal with, we also examined washed chalk, ground heavy spar, pure commercial potter's clay, sea salt, and Karlsbad salt for Becquerel radiation. The results were generally negative, traces being suspected in the case of the clay alone, but in any case it is inferior to the garden soil, as well as to the clay of Wolfenbüttel and the Loess. On account of the chemical similarity of radium and barium, we thought that we might expect to find some activity in heavy spar, as possibly traces of the first element might accompany the latter; the idea that Karlsbad salt is obtained from great depths of the earth induced us to examine it, whilst the sea salt, as an example of a soluble substance, might perhaps also contain radio-active constituents.

Ashes of plants which had grown on active earth also gave no appreciable Becquerel radiation.

The result of these researches is thus the proof of a certain radio-activity of the soil itself; this remains attached to the clayey constituents of the soil on treatment with dilute acids. We have not succeeded in further separating or completely isolating the active principle.

We were much pleased to hear of a confirmation of this result by Cooke, recently communicated by Rutherford (E. Rutherford, *Nature*, 1903, lxxvii., p. 511), according to whom a perceptible very penetrating radiation is said to be given off from brick.

Before attempting to concentrate the active substance distributed throughout the naturally occurring clay in only very small quantities, which is very difficult owing to the large amount of substance which must be employed, it was first to be considered whether this activity is chiefly primary, and not merely induced in the clay by contact with the air from the ground, in which case the origin of the activity in the latter would still remain unexplained. The behaviour of the clay towards acids, which agrees with that of the primarily active substances as well as the persistence of its activity, are certainly arguments against the last assumption, but still we did not think it unnecessary to examine generally whether neutral bodies, on being buried in the earth, i.e., after lengthy contact with the air of the ground, could assume an appreciable induced activity.

We used for this purpose ground heavy spar, whitening, pure nearly inactive potters' clay, and cotton. Each of these substances was wrapped in linen, and surrounded with a covering of iron wire gauze, and placed some 50 c.m. below the surface of the ground and left there at least four weeks. The wire gauze served to hold together the covering of linen, which became disintegrated in the earth, so that an adulteration of the substance with the soil was prevented. After being dug up, the heavy spar, whitening, and cotton showed no appreciable activity, but the activity of the clay was unmistakable. By its diminution in course of time, which moreover was different in different samples, it was clearly shown to be induced activity.

It is a noteworthy coincidence, which also rendered the further examination more difficult, that the clay which contains the primarily radiating substance which acts induc-

tively on the air of the ground, is itself excited to secondary radiation by this air.

We will now briefly report on some further experiments which partly supplement the above results and partly only confirm them.

If we brought some kilogrammes of earth into a closed space of about 40 litres capacity, and introduced a metal wire charged to - 2000 volts, after the lapse of some hours the induced activity might easily be proved by means of a leakage apparatus. If we sucked the air through a greater quantity of earth placed in a metal receptacle, and allowed it immediately after leaving the earth to enter the bell-glass which covered the leakage apparatus under the protecting wire gauze, it had always an abnormally high conductivity, which, however, disappeared after a few minutes, as soon as the current of air ceased. Hence, we must assume that the current of air in passing through the earth was ionised by its Becquerel radiation, in the same way as when it flows over an active Röntgen tube. The fact that we had to deal not with a simple ionisation of this kind, but rather with a taking-up of active emanation from the earth, was shown when we led the air before its entrance into the bell-glass through a metal tube, of diameter 1.5 c.m. and length 10 c.m., in the axis of which an insulated wire was stretched; the tube and the wire were connected with the poles of a high tension pile of about 1600 volts. The air thus flowed in a powerful electric field, by which either some free ions must be completely removed, or at any rate their number must be much diminished. However, no alteration in the loss of electricity resulted under the bell-glass, whether the electric field was established or not. Hence the phenomenon must be explained by the assumption that the air in passing through the earth takes up a small quantity of active emanation, which rapidly becomes inactive. If the air is allowed to pass through inactive material, such as heavy spar or chalk, neither action appears.

Following a suggestion of Herr Bodländer, of Brunswick, we also investigated the natural carbonic acid gas which is evolved from great depths of old volcanic soil, with regard to the active emanation it contains. We had sent to us a steel flask full of such natural carbon dioxide in the liquid state, from the carbon dioxide works of Schoor and Wolter, at Burgbrohl on the Rhine, immediately after it had been filled.

Although five days elapsed before the flask reached us, the gas when brought underneath the above-mentioned bell-glass was decidedly ionised. It followed on the one hand from the duration of the conductivity of the gas (which persisted for some days), not taking into account the defects of unipolar conduction, and on the other hand, from the possibility of secondarily rendering active a metal wire negatively charged and introduced into it, that we were not dealing with an excitation of electricity caused by the contents of the flask frothing out, or by the friction of the little drops on the opening, but with a genuine radio-activity. After the expiration of sixteen days the gas taken from the flask, which was still almost full, was inactive, and now behaved like artificial carbon dioxide which was generated from sodium bicarbonate and dilute sulphuric acid, and which was introduced beneath the bell-glass through a cotton-wool filter, in the same way as the natural gas.

The carbon dioxide arising from the earth thus carries with it an active emanation, exactly like the air contained in the capillaries of the earth. It would be interesting to investigate for the same property the gases arising from deep wells and thermal springs, immediately after their appearance at the surface of the earth.

In order to have always at our disposal a larger volume of the air charged with the earth emanation, we had a bell of strong sheet iron, of about 1½ cub.m. capacity, and tubulated at the top, buried with its lower edge 25 c.m. beneath the surface of the earth in the garden of our house. By diffusion, the equality of the activity of the air shut up

under the bell with that of the soil soon showed itself when the tube was closed.

The strong activity which we observed by means of wires which were insulated and negatively charged and sunk through the tube, led us to treat phosphorescing bodies in the same way, as we expected to observe in these distinct light phenomena.

When we introduced into the bell on a dark night a cardboard cylinder covered with Sidot's blende, which had been previously kept for days in the dark and showed no phosphorescence, and charged it negatively to 2000—3000 volts for some hours, on being taken out of the bell it showed a decidedly feeble phosphorescence, which, however, was plainly visible in a perfectly dark room.

On closer examination of the phenomenon, we observed that characteristic scintillating luminosity which has already been described by us, and by Sir Wm. Crookes (W. Crookes, *Nature*, 1903, lxvii., p. 522; J. Elster and H. Geitel, *Physikal. Zeitschrift*, 1903, iv., p. 439), and which is caused by the unceasing appearance and disappearance of countless points of light on the blende.

The thought at once occurred to us that these scintillating points represented the places at which negative electrons are hurled off from the radio-active layer covering the zinc blende. Sir Wm. Crookes, who observed the same thing when he brought a radium preparation near a screen covered with Sidot's blende, on the other hand regards them as the places at which the electrons hurled off by the radium hit the surface of the screen. Even if both conceptions are still purely hypothetical, we must regard ours as being more probably correct, because in our experiment, with the exception of the phosphorescing surface, no radio-active body was generally present, and thus a movement of electrons towards the latter did not generally occur.

(To be continued).

TWENTY-FIRST ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature, appointed by your body at the Montreal meeting in 1882, respectfully presents to the Chemical Section its Twenty-first Annual Report, covering the twelve months ending June 1, 1903.

Works Published.

"An Index to the Literature of Thorium (1817—1902)." By CAVALIER H. JOÛET, Ph.D. Smithsonian Miscellaneous Collections, No. —. Washington, City, 1903.

"References to Capillarity to the End of the Year 1900." By JOHN URI LLOYD (aided by) SIGMUND WALDBOTT. Bulletin No. 4 of the Lloyd Library of Botany, Pharmacy, and Materia Medica, Cincinnati, Ohio, 1902. 212 pp. 8vo.

The 665 "references" extend from 1519 to 1900; each is accompanied by a summary of the contents of the paper cited.

The Journal of the American Chemical Society. "General Index to the First Twenty Volumes, 1879—1898, and to the *Proceedings*, 1877—1879." Easton, Pa., 1902. 237 pp. 8vo.

Though issued anonymously the Preface bears the initials of E. W. Morley and O. F. Tower, and the labour was one of love. Accuracy of detail and adequate treatment on every page are its admirable features. Besides an index of Authors and an index of Subjects there is an index of Obituaries which is suggestive. Also an index of new books.

* Advance sheets from *Proceedings of the American Association for the Advancement of Science*.

Notes on Foreign Bibliographies.

"A Bibliography of Steel-works' Analysis," by HARRY BREARLEY, forms an Appendix to the volume entitled "The Analysis of Steel-works' Materials," by HARRY BREARLEY and FRED. IBBOTSON. London, 1902.

This Bibliography comprises 1858 references, which occupy more than 130 pages 8vo. The items are grouped under seven heads, besides minor sub-divisions; the literature is, however, very incomplete, being confined to four British journals.

"A Catalogue of the Library of the Chemical Society [of London]." Arranged according to Authors with a Subject Index. London, 1903. 8vo. 324 pp.

"International Catalogue of Scientific Literature." First Annual Issue [for the year 1901]. D. Chemistry. Published for the International Council by the Royal Society of London. London, 1902. Vol. II. Part I. June, 1902.

Works in Progress.

A Second Supplement to the "Select Bibliography of Chemistry," by Dr. H. Carrington Bolton, has been completed, and accepted by the Smithsonian Institution for publication. It brings the literature down to the end of the year 1902.

An "Index to the Literature of Cadmium" has been begun by Prof. Ernest N. Pattee, of Syracuse University.

An "Index to the Literature of Glucinum" has been begun by Prof. Chas. L. Parsons, of New Hampshire College, Durham, N.H.

An "Index to the Literature of Germanium, Gallium, and Indium," has been begun by Dr. Philip E. Browning, of New Haven, Conn.

Mr. Frank R. Fraprie, writing from Munich, Bavaria, reports substantial progress on an "Index to the Literature of Lithium, Cæsium, and Rubidium."

Mr. Benton Dales is engaged on an "Index to the Literature of the Yttrium Group of the Rare Earths." His address is Ithaca, N.Y.

Committee:—

H. CARRINGTON BOLTON (in Europe),
F. W. CLARKE (in Europe),
ALBERT B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

June 1, 1903.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.

(Continued from p. 18).

In an account of his expedition to Greenland in 1870, Prof. A. E. Nordenskjöld states (*Geological Magazine*, 1872, p. 355) that at the bottom of the holes in the ice he found a grey powder, to which he gave the name of cryoconite (*κρύος*, ice, and *κόμης*, dust); he found it on inland ice as well as on the shore ice; Nordenskjöld concluded that it was not derived from the disintegration of the rocks in the district, but from meteoric sources, especially as it contains particles of metallic iron bearing cobalt, copper, and probably nickel. Prof. Nordenskjöld describes it as occurring in layers some millimetres thick, and often conglomerated into small loose balls, and under the microscope as being principally made up of white angular transparent particles, intermixed with vegetable fragments as well as particles of what appear to be feldspar and augite.

Dr. G. Lindström obtained the following analytical results from a sample:—

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

Cryoconite.

Silica	62.25
Alumina	14.93
Iron sesquioxide	0.74
Iron protoxide	4.64
Manganese protoxide	0.07
Lime	5.09
Magnesia	3.00
Potash	2.02
Soda	4.01
Phosphoric acid	0.11
Chlorine	0.06
Water, hygroscopic, at 100° C.	0.34
Water and organic matter at a red heat	2.86

100.12

When long digested with strong sulphuric acid 7.73 per cent dissolved and 16.46 per cent when treated with strong hydrochloric acid. The organic matter seems to have been mainly due to the presence of various minute algæ. Particles of metallic iron have on several occasions been found in snow collected in places where there was no possibility of the iron having been derived from surrounding habitations.

In December, 1871, Nordenskjöld collected some snow near Stockholm, after five or six days consecutive fall, which on melting left a black soot-like residue containing metallic particles; to remove any possibility of doubt, Dr. Karl Nordenskjöld collected snow from off the ice of the Rautajerwi, on March 13, 1872, at Evoia, in Finland, separated by a thick forest from any houses (Dr. Walter Flight, "History of Meteorites," *Geological Magazine*, 1875, p. 157). The residue left on melting was soot-like in appearance, and under the microscope was seen to contain black carbonaceous particles, with yellowish-white granules and black magnetic grains, but the quantity was insufficient to determine the presence of cobalt and nickel. But snow collected by the Arctic expedition on August 8th, 1872, on the drift ice in Lat. 80° N. and Long. 30° E., yielded particles of metallic iron; also on September 2, in Lat. 80° N. and Long. 15° E., freshly fallen snow collected from the ice-field yielded from 0.1 to 1.0 m.grm. of black magnetic particles to the cubic metre of snow; iron, cobalt, and phosphorus were detected, and probably nickel was present also; the portion insoluble in acid contained fragments of diatoms and minute transparent angular particles.

Dr. Moss speaks of similar dust ("Voyage to the Polar Sea, in H.M.S. *Alert and Discovery*," Capt. Sir G. Nares, vol. ii., p. 61):—"Occasionally deposits of atmospheric dust were to be met with throughout the stratified ice, sometimes scattered in very minute points, which, when examined, proved to be air cells coated with the impalpable dust, sometimes occurring in comparatively conspicuous quantities in lines cutting the stratification and marking what had once been the bottom of a superglacial lake. Similar dust was to be found on the present surface of the floes, occasionally greatly magnified in appearance by the growth amongst it of an alga (*Nostoc aureum*). The dust often occurred in little granules, so that in mass it formed an oolite. . . . All the specimens of ice dust obtained by me from the floe bergs are undoubtedly the air carried débris of crystalline rock not traceable to the neighbouring shore."

On February 26, 1883, a fine dust was discovered in the snow in Trondhjem Amt, in North Norway. Dr. Reusch, of the Mineralogical Faculty of the Christiania University, found that it was not of volcanic origin as had been imagined, but that it consisted of fine particles of quartz sand, horn-blende, and talc, mixed with very fine particles of vegetable matter. The dust must have been carried a very long distance, the whole of the country having been for months covered with deep snow. The wind blew strongly from N.N.W.

In 1873, Prof. Nordenskjöld obtained rounded grains of metallic iron from hail which fell in Stockholm, other

observers had done the same as far back as 1821; Cozari had, in 1834, shown the presence of nickel in the iron brought down by hail.

Dr. Henry Rink, writing from Christiania, Norway, (*Nature*, Dec. 13, 1883) draws attention to the fact that the ice of icebergs which are made up of ancient snows ought to yield large quantities of Nordenskjöld's cosmic dust, although he had never observed its presence in such ice.

Reichenbach found traces of cobalt and nickel in the soil from the Lahisberg, in Austria, from the Haindelberg, Kallenberg, and Dreymarksteinberg, and nickel in the soil of the Marchfeld Plain (Dr. Flight, *Geological Magazine*, 1875, p. 162); the hills consist of sandstone and limestone, and are free from mineral veins. Haidinger suggested that impoverished soils when allowed to lie fallow acquire a fresh supply of phosphorus from such meteoric dust.

In the report for 1882 of the Committee of the British Association appointed for the purpose of investigating the practicability of collecting and identifying meteoric dust, &c., drawn up by Prof. Schuster, it is stated that the dust falls frequently observed in the Atlantic, the southern parts of Italy, and sometimes in the Red Sea, were at one time supposed to be of meteoric origin, but it has now been conclusively proved that the dust has its origin in the sandy deserts of northern Africa, whence it is carried by the winds often through considerable distances, the grosser particles falling down first, so that ultimately only the finest remain in suspension. Although these dust storms are of terrestrial origin, yet they carry magnetic and other particles which are of meteoric origin (see Tissandier's "Les poussières de l'air," Paris, 1877).

Amongst the magnetic particles found in the dust are some which are perfectly spherical; these have been found in the snow of Mont Blanc, at a height of nearly 9000 ft., and in the dust collected at various other places. The spherical particles have evidently been fused—no similar ones have ever been found in volcanic dust; the smoke from factory chimneys does contain similar particles, but such contain neither nickel nor cobalt, whereas Tissandier found both these metals in the magnetic particles collected at the Observatory of Saint Marie-du-Mont. "We are therefore driven to assume a cosmic origin to these particles."

Prof. Schuster examined the sand from the desert near the Great Pyramids and found magnetic particles present in the proportion of 1 in 144,000. Most were angular and evidently derived from magnetic rocks; but with them were also some perfect spheres of iron, similar to those described by Tissandier, and about 0.2 to 0.1 m.m. in diameter. Prof. Schuster naturally assumes that these spherical particles have been derived from the fused surfaces of meteorites in their passage through the atmosphere. He accounts for their non-oxidised condition partly by the fact that nickel iron alloys are less readily oxidised than iron, also that the fusion and separation from the meteorites probably took place in the upper regions of the atmosphere where the amount of oxygen is exceedingly small; at a height of only 200 kilometres the percentage of oxygen in the air is only about 0.8. He then refers to the presence of an unknown gas in the atmosphere indicated by a green line shown in the Aurora borealis spectrum—he assumes that this gas must have a very low density; supposing that it be as light as hydrogen, and that at the surface of the earth its quantity per cubic centimetre is only the one millionth part of the oxygen present in the same space, it would certainly escape all our methods of analysis. (1882). At a height of 200 kilometres it must exceed the oxygen in the proportion of 170,000 to 1; that is to say, at that height the atmosphere would practically contain no oxygen.

. . . Even if there are only minute quantities of free hydrogen on the surface of the earth, it may be in preponderating proportion in the upper regions.

Tissandier has shown how by burning iron wire in oxygen, we may often obtain iron spherules of exactly the same nature as those floating in our atmosphere.

"I have obtained similar spherules by using an iron file

as one pole of a dynamo machine, and passing the file over a copper wire connected with the other pole. The sparks consist chiefly of iron globules like those to which Tissandier attributes a meteoric origin; there are also spongy metallic masses, which present exactly the same appearance as the metallic iron found in the Sahara desert. The reason why they did not oxidise is no doubt due to the fact that a layer which was oxidised used up the oxygen in the neighbourhood of the few particles which escaped."

In 1883, the above Committee reported that three specimens of solid matter from snow and ice of the Himalayas were collected and examined. One from the Gamukdori Pass (lat. $35^{\circ} 5'$, long. $74^{\circ} 13'$) 13,400 ft., and two from the Shokari Pass (lat. 35° , long. $74^{\circ} 38'$) 14,700 ft. There is no human habitation near either of these places. The residue amounted to 0.1 grm. for the 25 cubic feet of snow boiled down in each case. All three specimens contained (1) spherical particles of magnetic oxide of iron, (2) small particles of metallic iron. These probably are of meteoric origin.

From the foregoing evidence, it is extremely probable that, as suggested by Haidinger, Reichenbach, and others, at all times and in all parts of the world there is a constant although imperceptible rain of such meteoric dust gently descending upon the earth's surface, the amount undergoing considerable variation, at times being much greater than at others, and from all accounts the fall in the month of November is the most abundant. This meteoric dust is apparently of the same general nature, and is probably derived from the same sources as the larger masses known as meteorites.

Roof dust, collected from the beams under the roof of the University, February 24, 1882. The proportion of magnetic material separated from one lot of this dust was 1.3 per cent, another lot gave 1.7 per cent. Most of it acquired a metallic lustre when ground in the mortar; some of this was fused with caustic soda, and the metallic residue was found to contain cobalt and nickel.

Mud from a Cistern.—Collected March 3, 1882, from a rain-water cistern (open) under the roof of the University building. When dried it yielded a grey coloured powder, containing sand grains, vegetable fibres, &c. The magnetic portion was fused with caustic soda to separate the iron oxides and entangled matters; the metallic portion contained traces of cobalt, but the indications for nickel were not satisfactory. The cobalt was present in less quantity in this than in the other roof dusts.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

THE Faraday Society, whose membership roll now numbers some 240 strong, held its first meeting on Tuesday evening, June 30th, at the Rooms of the Chemical Society, Burlington House, W., in the presence of a considerable audience. The President, Dr. J. W. SWAN, F.R.S., was unfortunately unable to be present, so the chair was taken by Mr. J. SWINBURNE, one of the Vice-Presidents.

The formal business of adopting the Rules that had been drawn up by the Council having been disposed of, the Chairman read a short Introductory Address by Dr. SWAN, in which he drew attention to the purpose and necessity of the Society. Dr. Swan's address will be printed in full in the *Proceedings* of the Society.

Mr. W. C. DAMPIER WHETHAM, F.R.S., then gave an abstract of his paper on "*The Present Position of the Theory of Electrolysis*."

The fact that the products of electrolysis appeared at the electrodes only led to the Grotthuss chain hypothesis. Faraday's laws suggest opposite convective streams of anions and cations. Hittorf's observations on the unequal concentration of the solution lead to the conception either of complex ions, dragging along salt or solution, or else

unequal velocities of the ions, whose ratio can be measured. Kohlrausch's measurements of the resistance of electrolytes enable the absolute velocities to be measured. The fact that the conduction of electricity in solutions obeys Ohm's law shows that the E.M.F. is merely directive, and that the ions have migratory freedom. The fact that ionic mobilities only vary slowly with dilution, while the conductivity of a dilute solution is proportional to the first power and not to the cube of the concentration, shows that the ions must be free of the solute molecules—not necessarily of those of the solvent. The osmotic properties of electrolytes lead to the same conclusion. A short consideration of conduction in non-aqueous solutions and in fused electrolytes completes the paper.

In the discussion which followed, Dr. R. A. LEHFELDT drew attention to the work of Jahn and Nernst on strong solutions.

Dr. T. M. LOWRY discussed the question of conduction in the Nernst filament, which he regarded as a mixture of electrolytes.

The SECRETARY read communications from Dr. SWAN and Prof. ARMSTRONG. The latter severely criticised the Dissociation Theory as involving necessary assumptions not in harmony with known facts. He hoped the Faraday Society would take no hasty decisions, but from the outset act with true scientific caution, and he applied for a fuller and more scientific use of the imagination in dealing with the phenomena underlying electrolysis.

In replying to some of Prof. Armstrong's strictures, Mr. WHETHAM remarked that although the early dissociationists unduly neglected the action of the solvent, that was by no means at present. "Free" ions means free from one another, not free from molecules of the solvent, and it is no part of the Dissociation Theory to deny that ions may be linked to the solvent, there being processes of interchanges allowing the ions to work their way through the solution.

Mr. JAMES SWINBURNE followed with a short account of his paper on "*Chlorine Smelting with Electrolysis*."

The process, which is an entirely new departure in the metallurgy of complex sulphide ores, consists, briefly, in treating the ores with hot chlorine, the temperature being of prime importance. This drives off pure sulphur. The mixed chlorides are then chemically treated by substitution, so that ultimately all the chlorine is combined with zinc, and, finally, the fused zinc chloride is electrolysed. The process is thus perfectly cyclical. Full figures of costs are given.

Mr. BERTRAM BLOUNT, who had seen the process at work, looked forward with confidence to the time when it would be applied on a large scale, yielding handsome profits.

Dr. O. J. STEINHART, in the course of an interesting speech, asked for particulars regarding the losses of chlorine and metals.

Mr. R. S. HUTTON remarked that if the process could be applied to such ores as the Sudbury nickel ores, it should prove of great value.

Mr. SWINBURNE, in his reply, stated that very little chlorine was wasted, while there was practically no point where loss of metal was possible. The difficulty as regards consumption of electrodes was got over by using cheap carbon in a preliminary electrolysis, until the fused zinc chloride was practically anhydrous.

Dr. LEHFELDT's paper on "*The Total and Free Energy of the Lead Accumulator*" was taken as read, and the discussion adjourned until the next meeting.

Dr. F. M. PERKIN exhibited and explained some novel forms of Electrodes for Electrolytic Analyses.

Change of Address.—We understand that, owing to the rapid increase of their business, Messrs. Geipel & Lange are removing to new and more commodious premises at 72a, St. Thomas Street, S.E., where they have also obtained a large warehouse for the purpose of increasing their stock of electrical apparatus of the descriptions which they are known to deal in.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 24, June 15, 1903.

Crystallisation of Slightly Soluble Bodies.—A. de Schulten.—The method of slow diffusion by which a number of crystalline bodies can be prepared can only be employed at ordinary temperatures. The author modifies this method so that it can be used where higher temperatures are necessary. For example, a solution of barium chloride and strong hydrochloric acid is placed in a flask heated on a water-bath, and sulphuric acid slowly dropped in, thorough mixing being insured by the convection currents from the water-bath. At the end of twenty-four hours crystals of barium sulphate begin to appear, and at the end of one month crystals of a measurable size can be collected. The same method can be employed for the preparation of celestine and anglesite.

Substitution of Zinc for Lead in Pigments.—T. L. Breton.—The author satisfactorily demonstrates that fresh paints containing lead do give off plumbic emanations, which may have grave effects on the health of those persons breathing them. He believes that from a hygienic point of view zinc paints should in all possible cases be substituted for lead.

Colloidal Silver.—M. Hanriot.—In a previous research the author showed that the commercial product known as collargol is not an allotropic modification of silver, but an alkaline salt of a true acid, collargolic acid. On seeking to purify this product by means of dilute acetic acid and ammonia, lylsalbinic acid remains in the mother-liquor. After four precipitations the proportion of the two substances becomes constant, silver 93.1 per cent and lylsalbine 6.1 per cent. The author also investigates the properties of this body.

Fusibility of Mixtures of Antimony Sulphide and Silver Sulphide.—H. Pélabon.—The curve of fusibility of mixtures of silver and antimony sulphides can be accurately constructed. It presents two maximum ordinates, which indicate the existence of two definite compounds, $Sb_2S_3 \cdot Ag_2S$ and $Sb_2S_3 \cdot 3Ag_2S$. It also presents three minimum ordinates differing very slightly from one another which correspond to three different eutectic mixtures.

Etherification of Sulphuric Acid.—A. Villiers.—The author performs experiments on the rate of etherification of sulphuric acid. Analyses were made of mixtures prepared in 1878, preserved in sealed bulbs at ordinary temperatures. His experiments seem to show that the limit of etherification, obtained by the action of alcohol on sulphuric acid, is the same whatever the temperature.

Certain Derivatives of Aminopyromucic Acid and Furfuranamine.—R. Marquis.—Nitropyromucic acid, when reduced by means of tin and hydrochloric acid, forms only succinic acid, carbonic acid, and ammonia. The author further investigates the reduction products of this substance, and obtains an amine derivative by the action of aluminium amalgam. He also prepares and examines the properties of ethyl aminopyromucate, $C_4H_2O \begin{smallmatrix} \text{NH}_2 \\ \text{CO}_2C_2H_5 \end{smallmatrix}$, ethyl acetaminopyromucate, $C_4H_2O \begin{smallmatrix} \text{NH}-\text{CO}-\text{CH}_3 \\ \text{CO}_2C_2H_5 \end{smallmatrix}$, ethyl benzoylaminopyromucate, acetaminopyromucic acid, $C_4H_2O \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{CH}_3 \\ \text{CO}_2H \end{smallmatrix}$, and acetyl furfuranamine, $C_4H_3O \begin{smallmatrix} \text{NH}-\text{CO} \cdot \text{CH}_3 \end{smallmatrix}$.

Action of Phosphorus Trichloride on Glycerin.—P. Carré.—Phosphorus trichloride behaves with glycerin in the same way as with glycol. A phosphorous ether of glycerin, $P_2O_6(C_2H_5)_2$, is produced, and a phosphorous ether of monochlorhydrine and glycerin, $P \cdot OH \cdot O_2C_2H_5 \cdot Cl$; these are immediately decomposed by cold water, giving the compounds $P_2(OH)_4 \cdot O_2C_2H_5 \cdot OH$ and $P(OH)_2 \cdot O \cdot C_2H_5 \cdot OH \cdot Cl$,

isolated in the form of their calcium salts. The action of phosphorus trichloride on glycol and glycerin results in the formation of ethers containing 2 mols. of phosphorous acid for 1 mol. of polyatomic alcohol, whilst the direct reaction of the acid on these alcohols only causes the fixation of a single molecule of the acid on to 1 mol. of glycol or glycerin.

Action of Sulphuretted Hydrogen on Methyl-ethylketone (Butanone).—F. Leteur.—When hydrogen sulphide reacts on a solution of ordinary acetone in strong hydrochloric acid at low temperatures the oxygen is replaced by sulphur and a substance called trithioacetone produced. The author modifies this method to render it applicable to butanethione for the following reasons:—(1) The presence of a certain quantity of water affects the reaction; (2) ketones being susceptible to alterations under the influence of hydrochloric acid, the products of their decomposition enter into the reaction. To avoid these two sources of error the author performs his experiments at a very low temperature and in the absence of water.

Two Isomeric Carbides of Campholene and Camphene.—L. Bouveault and G. Blanc.—The authors prepare carbides containing the group $=CH_2$ in order to compare their properties with those of the known carbides, campholene and camphene.

Synthesis of 2.2-Dimethylglutaric Acid.—E. E. Blaise.—Unsuitable for abstraction.

Atmospheric Formic Acid.—H. Henriet.—In a previous research the author showed the apparent existence in the air of a gaseous body formed by the union of a nitrogen base and an acid, probably formic acid. By a series of experiments described in this paper he completely identifies this to be formic acid.

Properties of Phenylglycolic Acid.—E. Chaner de Coninck.—When phenylglycolic acid is heated in presence of an excess of sulphuric acid or glycerin small quantities of carbonic anhydride are produced. The author investigates the mechanism of this reaction, and during this research discovers new properties of phenylglycolic acid.

The St. Louis Exhibition, 1904.—The Royal Commission for the St. Louis Exhibition, 1904, is specially desirous of securing a series of collective exhibits adequately representing the chemical industries of this country, and a sub-committee has been appointed to carry out the necessary arrangements. It is well known that other nations have already made provision for similar exhibits, and it would be most regrettable if Great Britain were placed in a less favourable position through the abstention of important members of the trade. No doubt in the circumstances of the case the benefits which manufacturers may be expected to derive from participation are mainly indirect, and it is perhaps necessary to appeal rather to patriotism than to business instincts in securing support, but it is gratifying to find so many of the leading firms of chemical manufacturers have already signified their willingness to exhibit, that a successful result may be regarded as already assured; much, however, yet remains to be done in this direction. For collective exhibits the Commission will, in addition to providing free space, make such arrangements as will largely reduce the expenses which exhibitors are ordinarily called upon to bear. Particulars of the course proposed to be adopted in carrying this into effect can be obtained from the Secretary of the Liberal Arts Committee, at the office of the Royal Commission for the St. Louis Exhibition, 1904, 47, Victoria Street, Westminster, S.W., and as it is needful that the Commission should as soon as possible be placed in a position to indicate the amount of space which will be required, it is hoped that those who have not already signified their intention to take part in the Exhibition will do so promptly.

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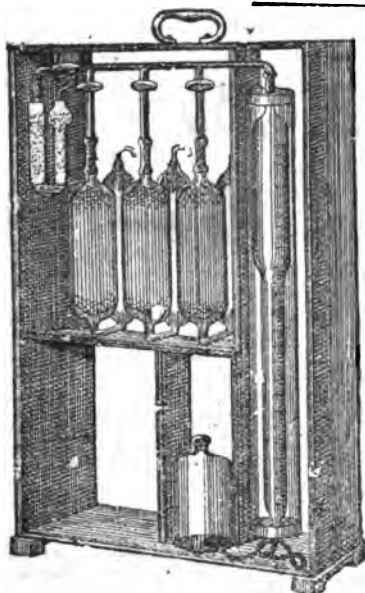
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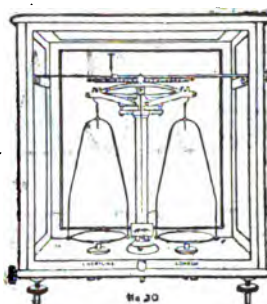
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2278.

ON THE SCINTILLATING PHOSPHORESCENCE OF SIDOT'S BLENDE CAUSED BY RADIO-ACTIVE EMANATION.

By J. ELSTER and H. GEITEL.

SOME days ago there appeared in an English daily paper (*Westminster Gazette* of March 20, 1903) a report of a paper read before the Royal Society by Sir William Crookes, on March 19th, entitled "The Emanations of Radium," which related to the peculiar kind of phosphorescence caused by the emanation of radio-active substances on a screen of Sidot's blende. Some time ago we noticed the phenomenon described by Crookes in the course of experiments which we had performed for the purpose of producing distinct phosphorescence by means of the active emanation contained in the air of the ground, and we meant to describe them very soon in a complete report on the results of further investigations of the activity of the air of the ground. As an addition to the above mentioned notice the following description of our experiments may now be of interest.

If we introduced into a dark space of about 1½ cubic metres capacity, which contained the radio-active emanation of the ground, an insulated screen of Sidot's blende, which had been kept in the dark for some days previously, and maintained it for about two hours at a negative potential of 2000 volts, it became luminous. On examining the screen more closely in the dark with a thoroughly well rested eye, we discovered the striking fact that the screen was not uniformly illuminated, but that the intensity of the light of the individual parts of the luminous surface was subjected to a constant change. If a screen thus rendered luminous is observed through a microscope it is seen that the scintillating of the screen is due to a number of separate luminous specks, each of which only flashes out momentarily.

As Crookes explained in the description of his experiment, when the luminous surface was examined by means of a magnifying glass, the effect was that of looking through a telescope at a group of stars, each of which flashed out only to disappear again at once in the black background.

As we have not for years had any radio-active substance in our laboratory because of our researches on the radio-activity of natural air, we have not been able to examine more closely the phenomenon in the case of strongly active substances, but we also obtained it, and indeed more clearly, with the air of the ground in a room situated at some distance from our laboratory, within a space of about 40 litres capacity, impregnated with thorium hydroxide (50 grms.). Finally, Giesel was kind enough to place at our disposal in his house all the emanating substance he had for the purpose of research.

On using the "emanation substance" (cf., F. Giesel, *Ber. d. Deutsch. Chem. Gesell.*, 1903, xxxvi., p. 342) the scintillating luminosity of the screen was also visible in an incompletely darkened space, and the aspect which the screen presented through a microscope was even more surprising; it could also be easily shown that this phosphorescent light is *not* extinguished by the influence of red light. This is a characteristic and easily understood difference between the phosphorescence produced by emanation and that produced by illumination. If the emanation substance wrapped in paper was laid directly on the (unelectrical) screen, the latter showed the same scintillating phosphorescence. A luminous screen of calcium tungstate after an exposure of about one hour was rendered lastingly

luminous, but the characteristic scintillating of zinc blende was not visible.

It must be mentioned that in the space prepared with thorium oxide the scintillating luminosity of the blende would be obtained, if with somewhat less intensity, after positive electrification. We have not carried out analogous experiments with the emanation substance.

In order to prove whether the flashing of the luminous points proceeded from little fragments of the active emanation which adhered to the screen itself, or from those fragments which had loosened themselves, and which radiated back on to the screen, we led a current of air over the screen. With the small speeds we employed no effect of the movement of the air was noticed. Moreover, the phenomenon remained the same whether the screen was closely pressed with its luminous side against a glass plate or not. This result would be compatible with the opinion expressed by Crookes, that the flashes of light are directly connected with the hurling off of electrons by the active surface itself. It would then appear remarkable that the screen of calcium tungstate did not exhibit the phenomenon. —*Physikalische Zeitschrift*, iv., 15, 439.

Wolfenbüttel, March 27, 1903.

COLOURED REACTIONS OF CHLOROFORM, BROMOFORM, AND IODOFORM.

By R. DUPOUY.

WHEN we react with chloroform on the phenols in the presence of dry potash, we obtain very brilliant colourations, very probably due to the formation of colouring matters belonging to the aurin group.

In this manner, with ordinary phenol we obtain a yellow colouration, with resorcin a bright red, and with naphthol a blue colouration.

I have tried this reaction with most of the phenols, and I have observed that by using isopropylmethylphenol or thymol, and by reacting with sulphuric acid on the product first formed, in the presence of potash, it was possible to obtain new colouring matters having characteristic absorption spectra. The following is the most convenient manner of proceeding:—

We place half a cubic centimetre of an alcoholic solution of thymol at 5 per cent in a test-tube; add a drop or chloroform and a morsel of caustic potash. This must be heated and kept at the boiling point for about half a minute. We then notice that the mixture has become yellow in colour, with a more or less pronounced reddish tint, according to the amount of chloroform used. Then we add, very carefully, a cubic centimetre of sulphuric acid, and again heat to boiling. A magnificent violet colour is then obtained, which is generally too intense to allow of direct examination with the spectroscope.

Therefore, a few drops of the violet liquid are poured into a little acetic acid, and a spectroscopic examination made, when we observe a spectrum which may be best compared with that of oxyhæmoglobin, characterised, as we know, by two bands situated in the green. However, this absorption spectrum differs a little from that of oxyhæmoglobin, as it is nearer the red end of the spectrum.

If instead of pouring the violet solution into acetic acid, we mix a few drops with water, we obtain a blue liquid, which gives a spectrum characterised by a band situated between the D line and the red.

As can be seen, this reaction differs completely from that which has been described by Vitali, and which consists of the use of a mixture of potash and thymol, which, under the influence of chloroform vapour, takes a violet colour.

Further, very small quantities of chloroform can be detected by means of this reaction, and for toxicological research we may use Vitali's apparatus, and, as recommended by the author (*Gazzetta Chimica Italiana*, 1881,

p. 489), draw in the chloroform in a stream of hydrogen for example. By letting the gas bubble through one cubic centimetre of an alcoholic solution of thymol, and proceeding as described above, we obtain a more or less intense violet colouration.

We may remark here, that in the absence of chloroform, sulphuric acid will occasionally give a very faint bluish colouration with thymol and potash, but the solution is entirely without spectral reactions. Further, to avoid all error, the sulphuric acid must be added only after the yellow colour has been first observed, and if this does not occur, it is useless to go on with the experiment.

Again, I have satisfied myself that all the coloured reactions of chloroform, which are described as characteristic in most treatises on analytical chemistry, succeed equally well with bromoform, and sometimes also with iodoform. In fact, the reaction I have just described can be obtained easily with bromoform, but more difficultly with iodoform. This circumstance must be borne in mind in the toxicological search for the trihalogen derivatives of methane.—*Bull. de la Société de Pharmacie de Bordeaux*, May, 1903, p. 140.

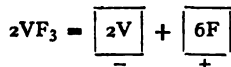
THE ELECTROLYTIC MANUFACTURE OF VANADIUM AND ITS ALLOYS.*

By GUSTAVE GIN.

THE principle of my process depends on the high conductivity of the trioxide of vanadium, and on the facility with which the trifluoride of vanadium is obtained, on attacking the trioxide with fluorine in the presence of carbon.

To illustrate how these characteristic properties can be utilised, let us suppose that we are electrolysing ferrous fluoride in solution, in fused fluoride of calcium, using an anode formed of an intimately agglomerated mixture of trioxide of vanadium and carbon, the cathode consisting of a bath of metallic iron.

The ferrous fluoride being decomposed by the current, the fluorine given off at the anode attacks the trioxide of vanadium, which gives up its oxygen to the carbon, while trifluoride of vanadium is formed according to the reaction $6F + V_2O_3 + 3C = 2VF_3 + 3CO$. The fluoride of vanadium formed goes into solution in the fluoride of calcium, and is electrolysed in its turn :—



The vanadium set at liberty combines with the metallic iron of the cathode, and at the anode there forms a fresh quantity of fluoride of vanadium, which is again electrolysed, so that the ferrous fluoride in question only serves to start the operation, furnishing the fluorine which acts as a vehicle for the vanadium to pass from the anode to the cathode.

I will now explain how I proceed in practice. Trioxide of vanadium, prepared by the calcination of vanadic acid in the presence of carbon, is mixed with a suitable proportion of retort carbon and powdered resin, so as to obtain a homogeneous, plastic paste by hot kneading. After being agglomerated in a special kneading trough, heated from the exterior, the paste passes to a mill, where it is crushed by heavy steel rolls. The paste leaving the mill is pounded, then by hydraulic pressure forced through a die similar to those used in the manufacture of electric light carbons. Finally we obtain prismatic or cylindrical rods, which are baked, in the absence of air, in very hot ovens.

Electrodes manufactured in this manner are kept pro-

tected from the air and moisture under a layer of some dry pulverulent substance, until they are required for use. I devised this means for the manufacture of these electrodes in conjunction with Dr. Gans, who supplied me with the vanadic acid necessary for my experiments.

The specific resistance of these electrodes was measured in the Laboratoire Central d'Electricité, at Paris, with the help of MM. Chaumat, Delon, and Petitalot, and was found to be 13,700 microhm-centimetres, at a temperature of 15° C. Electrodes made in the manner just described appear to be able to carry a current equal to 7/10ths of that used with carbon electrodes of the same sectional area.

The anode in my furnace consists of a bundle of electrodes made in the above manner; the cathode is formed of a block of steel. Certain special arrangements are necessary on account of the high fusing point of vanadium, and of the alloys containing it in any considerable quantity. For alloys with more than 25 per cent of vanadium, the cathodic section should be considerably less than the active surface of the anodes. A good return and a sufficiently fluid bath are obtained with a mean current density of 2 ampères per square centimetre of section of the anode, and 6 ampères per square centimetre of cathode, the electromotive force being from 11 to 12 volts.

As I observed at the commencement, the ferrous fluoride introduced into the bath at the beginning of the operation is only for the purpose of starting the electrolysis. Nevertheless, as a certain quantity of fluorine is lost by being transformed into gaseous tetrafluoride of carbon, on contact with the excess of carbon in the mixture forming the anode, it is advisable to compensate for this loss by adding a certain amount of ferrous fluoride from time to time.

The iron constituting the bath is added in the metallic state, by small quantities at a time, after each pouring of the ferro-vanadium. If no iron were added to the bath, we might obtain almost pure vanadium, but the casting of this substance is extremely difficult, and it must be taken from the furnace in the solid form. It is apparent that my process is applicable, under similar conditions, to the commercial manufacture of alloys of vanadium with other metals, such as copper, aluminium, manganese, &c. It suffices to replace the cathodic bath of iron by one of the metal it is wished to introduce into the alloy.

SOME PROPERTIES OF COLLOIDAL SILVER.

By A. CHASSEVANT and S. POSTERNAK.

COLLOIDAL silver is at present the object of numerous researches, on account of its recent therapeutic applications both in France and in other countries. At the last meeting of the Société Chimique, M. Hanriot made an interesting communication on Heyden's commercial collargol, which he looks upon as the ammoniacal salt of a definite acid, collargolic acid. One of us who was present at that meeting announced that we had prepared colloidal silver by a method analogous to that of Carey Lea, and that we were following up the examination of its chemical and physical properties.

For the purpose of preparing this colloidal silver, we followed the method adopted by Carey Lea for citrate of iron, with some modifications which gave us a much better return in its production. In this manner we obtained an amorphous product of a greyish metallic appearance with some iridescence.

This product, almost insoluble in water, dissolves to a very great extent in ammonia, giving it a deep brownish colouration.

It contains 90.08 per cent of silver, and a little iron and citric acid; it does not contain any albuminoid matter.

The properties of this compound are as follows :—

It is soluble in ammonia and in the alkalis; it is pre-

* A Paper read before Section X., at the Fifth International Chemical Congress at Berlin.

capitated from its solutions when we add a dilute acid in suitable proportion.

Its ammoniacal solution, poured into an excess of dilute acetic acid, gives an acid solution of a brown colour, retaining all the properties of colloidal silver, and does not become cloudy until after several hours. Nitric acid in excess decolourises it.

Carbonate of soda and carbonate of ammonia precipitate colloidal silver completely from its solutions.

Baryta water also causes complete precipitation.

Soda and ammonia in excess do not give any precipitate; but when these solutions are left exposed to the air, the carbonation of the alkalis causes the complete precipitation of the colloidal silver.

Sulphate of copper, when added in suitable proportion, precipitates the whole of the silver.

If we proceed comparatively with solutions containing the same amount of colloidal silver, but increasing amounts of ammonia, we observe that it is necessary to add increasing amounts of sulphate of copper in order to obtain the complete precipitation of the colloidal silver.

It appears to be necessary to add sufficient copper to saturate almost the whole of the ammonia present. The precipitate consists of a mixture of silver and hydrate of copper.

With nitrate of silver, sulphate of nickel, &c., we obtain analogous results.

We must not overlook a very curious property that has been already described. The more this product is triturated in an agate mortar, the less soluble it becomes in its solvents. A comparative experiment with a solution of ammonia containing 0.015 per cent of ammonia, with the initial product, and with the product ground for five minutes, gave different results. The first solution is of a deep brown colour, and contains a great deal of silver; the other is a bright yellow, and contains only a little silver but a good deal of impurities. It seems as if this mechanical action has changed the colloidal product to metallic silver, and has set free the impurities adhering to the physical particles of the colloidal silver.

The electrolytic phenomena are different, according to whether we pass the current through an alkaline or an acid solution of colloidal silver.

In the first case, we have observed that the colloidal silver is transformed towards the positive pole or anode, and that the brownish deposit which appears on the electrode re-dissolves in the ammoniacal water, giving a brownish solution.

When, on the other hand, we pass an electric current through an acetic solution of colloidal silver, the deposit occurs on the negative or cathode pole. It might be objected that the acetic acid has transformed the colloidal silver into acetate of silver, and that it is the basic silver that is deposited. Such, however, is not the case. The deposit on the platinum cathode is of a brown colour, and with dilute ammonia gives a brownish solution identical with the original one.

These phenomena of the transference of the physical particles which occurs alternatively at the positive or anode pole in the case of an alkaline solution, and at the negative or cathode pole in the case of an acid solution, are analogous with the facts already observed by other writers with other colloidal substances, facts already published by one of us (Posternak, *Ann. de l'Institut Pasteur*, 1901, p. 400, and Erratum, p. 451).

In our experiment with the electric current, colloidal silver behaves in the same manner as the flocks of albumin in Hardy's experiments (Hardy, *Zeit. Physik. Ch.*, vol. xxx., p. 285), and the flocks of hydrate of iron, silica, &c., in the experiments of Lindeer and Picton (*Chem. Soc.*, 1897, vol. lxxi., p. 568). We must admit, therefore, that the different direction given by the electric current to the physical particles of colloidal silver in acid or alkaline solution, is not due to the chemical properties of this body, but to the electrostatic charges communicated to its particles by the most mobile ions present in these solutions.

A positive charge in the case of acid liquids (the most mobile ion being H^+), and a negative charge in the case of alkaline solutions (the most mobile ion being OH^-).

These facts have been demonstrated already by Posternak in the case of colloids, and have just recently received confirmation in a research by Knoblauch.

The summary of the reactions we have just described enables us to state that the product we have prepared possesses the properties of a colloid, and that a definite chemical function cannot be attributed to it, since we know that the solubility of colloids in acids and alkalis does not suffice for us to affirm the basic or acid nature of their functions.

If we admitted that colloidal silver was an acid, because of its solubility in ammonia and in the alkalis, it would be necessary also to admit that it is a base because of its solubility in acetic acid.

It is difficult to comprehend how the ammoniacal salt of colloidal silver, soluble in water, could be precipitated by carbonate of ammonia or carbonate of soda; and again, why in acetic solution the radical with an acid function (colloidal silver) of the ammoniacal salt goes to the negative pole, which is contrary to what we know of the electrolysis of salts in acid solution.

It must be well understood that all the above facts apply only to the product we have prepared; it would be interesting to compare this colloidal silver with commercial collargol, which, among other impurities, contains an albuminoid substance which may mask or modify the reactions of the mineral colloid.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 11.

RADIUM AND HELIUM.

THE following paragraph appeared in *The Times* of the 20th inst :—

"A paper bearing in a remarkable way on the connection between these two elements, which is now exciting so much interest, has been received for publication by the Royal Society from Sir W. and Lady Huggins. Prompted, in fact, by theoretical ideas, they attacked the problem of the spectroscopic analysis of the light emitted directly by a radium salt at ordinary temperatures. Preliminary visual observation seemed to show traces of bright lines in a continuous spectrum. Preparations were accordingly made for photographic record by means of a small quartz spectro-scope constructed some years ago for use on very faint celestial objects. After several trials, a spectrum consisting of eight definite bright lines in the ultra-violet, entirely different from the spark spectrum of radium, and some faint lines together with a very faint continuous spectrum, was obtained by seventy-two hours' exposure to the glow. The lines were of some breadth, on account of the wide slit that had to be employed in order to admit sufficient light; but it was found possible to measure their wave-lengths within an error of two in the fourth figure. On a comparison of this spectrum, so different in type from an ordinary phosphorescent spectrum, with the recorded measurements for helium, it appeared at once that four, and perhaps five, of the eight lines agreed with lines of helium within the uncertainty of the measurements. Another line, that of highest refrangibility, agrees with a line in the spark spectrum of radium itself, which, however, has not been recorded by other observers; the two other lines, the lowest, have not yet been traced.

"It will be remembered that last year Prof. Rutherford produced striking evidence for the view that, in the very slow break-up of radium that is concomitant with its radio-activity, the inert gas helium is one of the products formed. Recently, Sir W. Ramsay and Mr. F. Soddy have succeeded in detecting helium by the spectroscopic in the

gases extracted from a radium salt. If, as the present observations indicate, the radium salt shines spontaneously in the dark largely by light belonging to the different element helium, another important step is gained in elucidating the nature of the instability of such chemical elements of high atomic weight and the radio-activity associated with it."

Speaking at the Dinner of the Society of Chemical Industry at Bradford, on the 16th inst., Sir WILLIAM RAMSAY, President, described a new development of the radium mystery.

For some time (he said) two very distinguished young scientists belonging to Canada—Prof. Rutherford, of Montreal, and Mr. Soddy, who was now working in his laboratory—had been investigating the properties of those mysterious elements which had the power of discharging an electroscope when they were brought near it. His audience were aware, no doubt, that that property was first discovered for uranium by M. Becquerel, of Paris, and not long afterwards Mme. Curie discovered the wonderful element, radium. Messrs. Rutherford and Soddy discovered that thorium, an element not far removed from radium and uranium, gave off what they called an emanation, or what might be called a gas—a substance that could be moved from place to place, which could be condensed by cooling at a sufficiently low temperature, but which was most remarkable as a substance which discharged a loaded electroscope, and also as a substance which shone in the dark. They pointed out that radium gave out a similar emanation or gas continuously, that any salt of radium—radium bromide was what was generally used—but any salt of radium if allowed to stand for a while accumulated a further quantity of gas which could be removed with a pump or by washing it out with another gas. This very curious substance lost its properties on standing. If it was allowed to remain for four days it had parted with half its power to discharge an electroscope, and became, if looked at in the dark—as far as one could judge by the eye—half as luminous. And as time went on it lost its power of discharging electricity, and also its luminosity, until at length there was nothing left. There appeared to be no residue as far as one could tell. Mr. Soddy had done him the honour of coming and working in his laboratory, and as he (the speaker) had had some little experience in dealing with small quantities of gas, they laid their heads together, and had contrived to examine this emanation or gas given off by radium. He might tell those who did not know, that radium was very expensive, because it was a very rare substance, and that £25 would buy a very small quantity indeed—less than one grain. They managed to scrape together the needful, and invested in as much radium as they could get—all that there was in the market at the present moment.

Having examined this gas (Sir William continued) we found, to our astonishment, the other day that the emanation contains a quantity of helium, a light constituent of the atmosphere. I don't wish to imply that the emanation is helium, for it is not. The gas was first passed through a tube cooled with liquid air, in which the emanation stays behind, being condensed at that low temperature. But the other gas passes through this cold tube, and when collected in a microscopic Pluecker tube—what we call a vacuum tube—it shows undoubtedly the whole spectrum of helium (applause). It is impossible to forecast what this implies, but you must remember that the radium bromide which we have obtained, prepared, no doubt, by the same process which the Curies used, namely, the decomposition of pitchblende, a uranium mineral, with precipitation of barium by means of sulphuric acid, and with it radium, and separation of radium from barium by fractional crystallisation—that this radium obtained from pitchblende can hardly be supposed to have retained any helium through all those manifold operations. And it

would follow that the helium must be generated from the radium or from the gas—the emanation—which the radium gives off. At present I am as much in the dark about it as anyone. I merely chronicle the fact that there is undoubtedly a production of helium continuously from radium.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, July 9th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 2nd to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, 198 were found to be clear, bright, and well filtered; four samples were recorded as clear but dull, and one was very slightly turbid.

The rainfall at Oxford during June has been remarkable in more ways than one; the actual amount of rain measured was 5.58 inches, a larger amount than we have ever recorded before in one month, but this rain fell on ten days only, and by far the greater portion of it between the 8th and the 16th inst., and no rain fell at all after the 19th. The average fall for the month is 2.10 inches, so we have an excess for June of 3.48 inches, which added to the previous one of 4.35 inches, gives a total excess for the first half of the year of 7.83 inches, or 72.4 per cent on the thirty-five years' average.

Last month the total excess of rainfall amounted to 49.9 per cent on the thirty years' average, so that during the month of June actually 22.5 per cent, or an amount approaching one-half of the previous excess of rain, has fallen in the valley of the Thames. Such an amount of rain is altogether exceptional in our twenty-two years' experience. The result has been that, as we pointed out in our report for May, the proportion of vegetable matter in solution, and therefore the colour of the water, are both quite exceptional for the summer months. Nevertheless, the general filtration has been adequately and effectively performed, as is shown by the following bacteriological results. (See next column).

Of the 269 daily samples taken from the filter wells of the Metropolitan Water Companies, twelve samples, or 4.4 per cent were sterile. There were fifteen samples, or 5.5 per cent, containing more than 100 microbes, and of these, eight samples contained more than 150 microbes per c.c. The fifteen excess samples contained an average of 247 microbes per c.c.: in May seven excess samples contained an average of 124.

Our bacteriological examinations of 342 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 243 others from special wells, standpipes, &c., making a total of 585 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	151
New River, filtered (mean of 69 samples) ..	7
Thames, unfiltered (mean of 23 samples) ..	10337
Thames-derived water from the clear-water wells of seven Thames-derived supplies (mean of 175 samples) ..	42
Ditto ditto highest	588
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	474
River Lea, from the East London Water Com- pany's clear-water wells (mean of 25 samples) ..	28

Although therefore the mean number of microbes in the filtered supply is higher than in May, the increment is not excessive, and moreover was not generally distributed over the whole area of supply.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.
(Continued from p. 34).

Roof Dust.—In March, 1882, Mr. Russell, Government Astronomer, collected for me some dust from the roof of the Sydney Observatory. From 493 grms. of this the magnet extracted 48·5 grms., or roughly 9·8 per cent; but as this evidently contained much entangled non-magnetic matter, it was boiled with caustic soda and repeatedly extracted with a magnet under the soda solution. The proportion of magnetic matter to the original dust was then found to be only 1·5 per cent. Under the microscope it had the appearance of Fe_3O_4 , but with it were some lustrous steely looking flakes. The magnetic material was found to contain both cobalt and nickel.

The comparatively large quantity of magnetic matter in the three Sydney dusts is probably due to the lighter materials having been gradually removed; i.e., the two dusts had been subjected to a process of vanning by air currents, and the mud had been concentrated by the water flowing in and out of the cistern.

These dusts collected in Sydney confirm the results obtained by M. Tissandier and others; it was thought sufficient to ascertain the presence of cobalt and nickel. The quantitative analyses were not undertaken, as they would have occupied a great deal of time, and would have afforded but very little more information.

Meteoric Dust from Uralla, collected by Mr. Cleghorne, December 14, 1883. A fine reddish dust with some angular grains; most are clear and colourless, but some are yellow or red. Like the other red dusts, it contains granules of concretionary calcium carbonate, which dissolve with effervescence in acetic acid, also particles of charcoal or decayed vegetable matter. The average size of the grains is from 0·01 to 0·02 m.m.

Analysis.	
Moisture at 100°	4·25
Silica	70·60
Iron sesquioxide	4·66
Alumina	18·74
Lime	0·70
Undetermined	1·05
100·00	

Mr. Cleghorne, in writing from Uralla, on December 14, 1883, says: "I enclose herewith a sample of dust which fell in this neighbourhood yesterday (Thursday) morning. About 5 o'clock on Wednesday evening we had a sudden and severe thunder-storm, with much rain and some hail; the evening was clear moonlight, but during the night we had several thunder showers, especially towards morning—from early morning to about 11 a.m. there was a very singular yellow coloured fog, all vegetation was sprinkled with fine yellow dust, it could be easily gathered from iron roofs, but it appears to have fallen before the showers of rain in the morning, as it had been washed into the gutters of the roofing, and partially washed from the leaves, some samples of which I also enclose. I have not yet been able to learn how far this unusual occurrence extended."

The foregoing part of this paper, except the quantitative analyses, was written about 20 years ago, but put by pending the completion of the analyses; since then other samples of atmospheric dust have come into my possession and the results of their examination are now given.

Meteoric Dust from the Barrier Range, near Broken Hill. Collected by Mr. C. W. Lloyd, in 1896. Of a reddish colour, rather coarser in grain than the dusts from Menindie, Moruya, &c. The average size of the particles is 0·07 m.m., or 3/1000ths inch. It appears to be made up principally of water-worn quartz grains, stained with iron oxide, with some charcoal or carbonaceous fragments, also calcareous particles (concretions and fragments of shells), and a few black non-magnetic mineral fragments.

Analysis.	
Moisture at 100°	2·30
Silica	79·10
Iron sesquioxide	2·97
Alumina	10·58
Lime	2·00
Magnesia	traces
Loss on ignition	3·00
99·95	

Meteoric Dust, Pambula.—This sample was collected by Mr. H. Forde, on October 5th, 1899, who states that it fell all over the township of Pambula (land district of Eden), and bore the appearance of a thick red fog. This dust is an extremely fine and impalpable powder of a pale brownish tint. The average size of the particles is less than 0·01 m.m. As it apparently does not differ materially from the others, it has not been analysed.

Meteoric Dust from Menindie.—This specimen was forwarded to me by Mr. H. C. Russell, the Government Astronomer, on November 23rd, 1899, who stated that it had been collected by a friend during a recent red dust rain storm, who took great care to get it pure; on drying (under cover to keep the ordinary dust out of it) it split up into pieces and curled up like a dried clay. Of a reddish colour; under the microscope it appears to be composed principally of rounded quartz grains, some of which are reddish from a film of iron oxide. The average size of the particles is 0·25 m.m., or 1/100th inch. Mixed with the dust are some small pieces of calcium carbonate (concretions and fragments of shells) also some fragments of soft black readily combustible carbonaceous material, which may be water-logged charcoal, from bush fires or decayed wood; there are also a few particles of black mineral matter, probably chromite, but not yet examined.

Analysis.	
Moisture at 100°	0·85
Loss on ignition	2·20
Silica	89·15
Iron	1·06
Alumina	6·39
Lime	0·80 = 1·43 CaCO_3
Magnesia	traces
Alkalis	traces
100·45	

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

The following from Victoria is added for comparison :—

"Red Rain" Dust.—Some of this dust was collected at Moonee Ponds, near Melbourne, from a shower which fell on December 27, 1896, over Melbourne and a considerable area in Victoria, and was examined by Mr. T. Steel, F.C.S. ("Report Aust. Assoc. for Advt. Science," Sydney, 1898). He regarded it as a sample of ordinary surface soil, derived from the weathering of volcanic rocks; it contained diatoms, &c., such as are usually found in fresh water deposits.

Dried at 110°. Moisture in air-dried sample = 6.09

Loss on ignition	10.70
Sand, insoluble and undetermined ..	66.23
Alumina	15.16
Soluble silica	0.75
Ferric oxide	4.68
Ferrous oxide	0.50
Lime	1.36
Sulphur trioxide	0.62

100.00

For the sake of comparison the following analyses of dusts of undoubted volcanic origin are added; it will be seen at once that the atmospheric or so-called meteoric dust is very different in composition. Under the microscope the differences are still more strongly marked.

Krakatoa Ashes, collected at Batavia. Analysed by A. Sauer (*Fahrh. f. Min.*, 1884).

SiO ₂	63.30
TiO ₂	1.08
Al ₂ O ₃	14.52
Fe ₂ O ₃ }	5.82
FeO }	
CaO	4.00
MgO	1.66
MnO	0.23
Na ₂ O	5.14
K ₂ O	1.43
Loss on ignition	2.17

99.35

Volcanic Dust, Barbados (*Geol. Soc.*, May 25, 1902; *Nature*, June 5, 1902). From the recent eruption, the ash consists principally of a plagioclase felspar allied to labradorite, hypersthene, monoclinic augite, and magnetite. The following analysis was made by Dr. Pollard :—

SiO ₂	52.81
TiO ₂	0.95
Al ₂ O ₃	18.79
Fe ₂ O ₃	3.28
FeO	4.58
MnO	0.28
(CoNi)O	0.07
CaO	9.58
MgO	5.19
K ₂ O	0.60
Na ₂ O	3.23
P ₂ O ₅	0.15
SO ₃	0.33
Cl	0.14
H ₂ O (105°)	0.20
H ₂ O (above 105°)	0.17

100.35

Volcanic Dust from Mont Pelée, Martinique, collected from the deck of the S.S. *Roddam*, the only ship which escaped from St. Pierre (*CHEM. NEWS*, lxxxv., p. 282). Dried at 105°.

Silica	53.40
Alumina	21.00
Iron sesquioxide	9.50
Lime	9.70
Magnesia	2.00
Na ₂ O	2.33
K ₂ O	0.85
SO ₃	0.90
P ₂ O ₅	0.25

99.93

The following hitherto unpublished accounts of falls of meteoric dust and dust fogs in New South Wales are, except the first, selected from a large number kindly placed at my disposal by Mr. H. C. Russell, F.R.S., Government Astronomer; they are of interest as showing the conditions under which some of the dusts were deposited.

One of the earliest accounts of dust storms in Australia is given by Strelecki in his "New South Wales and Van Diemen's Land," published in 1845. He says :—

"In sailing from New Zealand to New South Wales in the *Justine*, I was prevented making the harbour of Port Jackson for two successive days by the violence of the hot wind. The distance from the shore, on the parallel of Sydney, was sixty miles, and the heat exceeded 90°. The lee sails and reefs of the *Justine* were covered with a quantity of impalpable dust, which was at first mistaken for ashes, but on examination proved to be sand, containing one-fourth of aluminous and three-fourths of siliceous and metallic matter. Those who shape their course to the East Indies, by way of Cape Verde Islands, may have seen the same effect produced by the north-east African hot wind."

The following account was addressed to Mr. Russell :—

"Times Office, Murrumbidgee, Oct. 21, 1876.

"So far as I have been able to ascertain, the dry fog was first seen in the vicinity of Tamworth, at about sunrise on the morning of the 12th instant. In the various weather notices of different journals published north or west of that town, no mention is made of the phenomenon, such as would be expected had its appearance been observed in the districts they represent. The *Tamworth News* refers to it as obscuring the horizon from north-east to south-west, and as being the result of the refraction of the solar rays on passing through the depressed exhalations from the moistened earth. In this neighbourhood the conditions under which the fog appeared were quite different, its direction being rather from north-west to south-east, and its existence altogether independent of "moistened earth," the preceding night having been too mild in temperature to produce a very copious fall of dew. With these exceptions the accounts coincide in the general representation of the event already furnished.

"Its appearance and disappearance were alike sudden, considering the immense extent of country it appears to have covered, and its rate of progress was exceedingly rapid. At half-past five a.m. on Thursday, the valley of the Page was as clear as usual on fine mornings, but on the ranges a peculiar dense mist, in colour precisely like a dust-cloud, was seen advancing quickly towards the town of Murrumbidgee. At 6 o'clock the whole of the valley with the town and the surrounding mountains were enveloped in the murky haze, the atmosphere became oppressive as though a heavy thunderstorm were at hand, and the sun was so obscured that it could be viewed without the slightest inconvenience by the naked eye. No disagreeable odour accompanied the fog, but it caused a sensation similar to that experienced during the first downpour of rain upon a dusty surface, that oppressiveness to the senses generally that a continued fall of rain would be likely to relieve. In fact, had it not been for the strangely impalpable nature of the fog, it would have been considered as an extraordinary diffusion of dust in the atmosphere, consequent upon strong winds. No inconvenience

was occasioned to the eyes, the only discomfort being the comparative sultriness of the morning and the sense of oppression experienced. No dust was left by the fog, nor the slightest moisture; it remained for many hours a perfectly dry, dense, dusty looking mist enwrapping every object in obscurity for many miles around. Shortly after half-past eight a.m. it left the Page valley, and proceeded towards the south, driven before the wind which rushed along the passage between the mountains with great force. The general direction of the wind was nearly direct from west to east, but as usual in the valley its course locally was determined by the position of the mountains, and the fog in the lowest lands was driven off to the south at the time already mentioned, while a portion of it lingered about the hills until nearly midday; at the head of the Page, I believe, it was discernible in the afternoon.

"At Scone, twenty-five miles south of Murrurundi, the fog made its appearance shortly before 8 a.m., while Murrurundi was still enveloped in its mist. A gentleman resident in this colony for upwards of thirty years, and a very shrewd observer of the weather, happened to travel from Murrurundi to Scone during the continuance of the fog, and he states that he was surrounded by it the whole way. He started on the journey about an hour after the fog made its appearance here, and his impression was that the mist was travelling at a rate of more than fifteen miles an hour. After leaving the valley of the Page, the wind was found to be blowing stiffly from the west, but the fog remained at Scone until nearly midday, when it gradually cleared off.

"The manner of its disappearance from Murrurundi was somewhat sudden, and would give the impression that it was carried by the wind over the country at a considerable speed. But the fact of it having remained amongst the mountains so much longer, leads me to think that it was driven out of the valley as from a narrow passage by the increased force of the wind when compressed within the limits of the pass. The occurrence of winds in this part of different directions and force from those in more open country is too common to need further mention, and it is tolerably certain that in the open country the fog was not so visibly and directly influenced by the wind as it appeared to be at Murrurundi. It should be mentioned that the wind was not noticed until some time after the fog made its appearance; the air was at first still, heavy, and oppressive, but afterwards the wind rose quickly, with frequent gusts, which swept great quantities of dust along the main road, giving colour to the supposition of some persons that a similar wind had blown during the earlier part of the morning, raising clouds of dust, the finer portions of which were still being carried by upper currents of wind across the country. But this is only one of many explanations invented for the occasion, and without any knowledge of the extent of the fog; allusion to some others more distant from reason and experience is made in one or other of the extracts enclosed.

"At Singleton the fog appears to have been witnessed at seven o'clock, about half an hour later than at Murrurundi, while at Scone, nearly half-way between, it would appear to have not been observed until a later hour than either—between half-past seven and eight o'clock. If I remember rightly, its appearance at the Paterson was still later, and no record of its having been observed further south or east is procurable here. The Maitland and Newcastle papers make no editorial comment upon it, nor with regard to Newcastle journals has any reference whatever to the occurrence been made. I may add here that, as already stated, the Gunnedah, Armidale, Glen Innes, Tenterfield, and other papers published in the north and west, seem to have taken no notice of the phenomenon, so that thus far observation is limited to the districts between Tamworth and the Paterson.

"In answer to your question, 'Did it leave any dust; if so, was any collected?' I may repeat that no dust was observed to fall from the dark mist, but the occurrence of high winds raising the usual clouds of dust from the roads

would hinder the attempt to distinguish between the dust deposited from either source unless the difference were very clearly marked. I am alluding now, of course, to observations made at positions within the reach of dust driven from the roads by high winds. In remoter places, I am informed, the only peculiarity remarked in the fog was its singular dryness, together with its discolouration, as compared with usual mists.

"From the best enquiries I have been able so make, such a fog has never been witnessed before by residents in the districts visited, and the subject has been very generally canvassed in the circles of the 'oldest inhabitants.' A general impression that it was the precursor of blight or an insect visitation existed, probably owing to the fact that some persons of years and education adopted this view of the occurrence and injudiciously (I think) gave their ideas to the less informed and more impressionable of the residents. All were agreed, however, that the phenomenon had never been witnessed here before, whatever might be the opinions entertained respecting its origin or consequences.

"The time at which the fog first made its appearance in the different districts mentioned, seems to involve the subject in more difficulty than it presented at first to myself, but by correspondence I shall endeavour to obtain further and more precise information upon this point. After perusing your interesting paper and Humboldt's remarks upon dry fogs, with the more remote phenomena recorded by the Roman poet, I can find no parallel to this occurrence excepting in the appearance of cosmical meteoric dust, hypothetically alluded to in your concluding remarks."—
H. JONES.

"Times Office, Murrurundi, Nov. 7, 1896.

"From enquiries made since my last, I have gleaned a few particulars, which, though imperfect, may be worth communicating. The most important of these have been supplied by Mr. George Armstrong, a gentleman of very extensive colonial experience, at present residing at Walcha. He informs me that the dry fog of the 12th ultimo was noticed near Bendemeer on the morning of that day, about six o'clock. He was out with some assistants looking after stock in the vicinity of Bendemeer, between that town and Surveyor's Creek, when his attention was attracted by an apparently heavy, wide-spreading cloud of smoke rolling over the distant mountains. He directed the notice of those who accompanied him to the strange appearance, and the impression left upon their minds was that an immense bush fire had occurred on the hills, causing the smoke they imagined to be covering the mountains. They rode in the direction of the mist, and soon discovered that its origin and nature were widely different from those already mentioned. In short, they found it to be a dry fog, of such an extent and density, however, as to render it quite singular. Mr. Armstrong is a native of South Australia, of which colony his father and uncle were amongst the earliest pioneers, and he has therefore the benefit of at least forty years' clear knowledge of the seasons and phenomena witnessed in these colonies. According to his account, these dry fogs, though not common, have occurred several times within his recollection, but have never had nearly so wide a range as that of last month. Many years ago he encountered one of these fogs at the head of the Wilson River, in the meridian of Capricorn; he was then engaged in driving stock, I think, and when approaching the Valley of Lagoons, witnessed a phenomenon similar to those under notice, but of a comparatively local character. More recently, while travelling with a large flock of sheep, he noticed a dry fog at Goonoo Goonoo, a station of the Peel River Company, near Tamworth, but this also was of limited extent. The most notable of these occurrences, he says, occurred in South Australia in 1836, in the month of April. That colony had only just been formed at that time, and the phenomenon excited a good deal of apprehension in the minds of the settlers. There can scarcely be any evidence I imagine, of the extent over which the fog of 1836 was observed, as the colony had not then been opened up. The aborigines

associated the occurrence with some mischievous event, the nature of which they could not define. I omitted to mention that at Bendemeer there was no wind perceptible immediately before the fog appeared, but shortly afterwards a slight westerly wind sprang up. The direction in which the fog appeared to the view from Bendemeer was about south-west by west. The fog appeared to annoy the horses the party were riding. The fog covered the Swamp Oak Creek, Surveyor's Creek, and intermediate country.

"This is the extent of my information respecting the fog as it appeared at Bendemeer, but Mr. Armstrong has promised to furnish me with memoranda of this and other dry fogs which he has preserved. If I should receive them I need not add that they will be speedily forwarded to you.

"A friend who visited Clarence Town a day or two after the 12th ultimo, tells me that the fog was the topic of general remark during his stay. In that locality it is said to have presented a dull grey leaden hue, but otherwise preserved the peculiarities noticed elsewhere.

"At Bellevue, near Scone, a number of aborigines are located, and the fog has not passed them without observation. They take it to be a sign of approaching drought, and they tell of similar appearances having been noticed in past years. This at present is all the additional information I have to offer. I am expecting more in answer to letters sent to different persons likely to have observed the phenomenon."—H. JONES.

"P.S.—I have not been able to secure any dust, or learn of any having been deposited by the fog or whatever the phenomenon should be termed."

"Yabtree, Gundagai, Dec. 23, 1880.

"Having seen your paragraph in *Herald* re dust storm that occurred on Wednesday, 15th instant, will state herein the storm as observed here. Yabtree is on the Murrumbidgee, about equal distance from Gundagai and Wagga. About 1 p.m. on the 15th the sky became overcast, sun obscured, and some hills about two miles away partially so; they had the appearance of heavy rain falling; wind strong from about W.N.W.; in a few minutes the dust made its appearance, it was very fine. At first I thought it was smoke coming from bush fires, and although the house was closed, in a few minutes everything inside was covered with fine dust. The storm lasted until about 6 p.m., the sun having been invisible the whole time and wind in nearly same direction; then a few drops of rain fell, the wind fell away to almost a calm, and sky partially cleared, only few rain clouds passing slowly to east; a few more drops of rain fell about 8 p.m., after which the night was a clear one. There are no roads near Yabtree from which the dust could come, so I came to the conclusion that it was due to a storm, and felt disappointed by not seeing any remarks thereon in telegrams in Thursday's *Herald*, except from one station, Euabalong on the Lachan River, about 200 miles W.N.W. from here; the direction from here to where the *Potosi* passed the mud shower, is about E.S.E., so the Euabalong, Yabtree, and *Potosi* storms were most likely likely one."—R. F. HORSLEY.

"Tumut, N.S.W., Dec. 23, 1880.

"I see by your letter in the *Sydney Herald*, dated Dec. 20, that you are anxious to collect all the information you can get as to the showers of mud that fell on board the S.S. *Potosi*, and also at Moruya, on Wednesday, the 15th December. At Tumut the morning opened calm and hot; about 10 a.m. the wind began to rise and whirled the dust along in thick choking clouds, which gradually mounted higher and higher into mid-air until all the surrounding hills were blotted out, or only seen occasionally, as though a heavy thunderstorm was raging in their vicinity. Thermometer standing, 12.30 p.m., at 94° in the shade, in about the coolest spot to be found in Tumut, viz., large open shed at the Brewery, with a thick bark roof, where the beer is cooled before going into the casks; on this occasion the cooling table was covered with cold water to keep the seams tight while no brewing was going on.

"As Wynyard Street was the main channel of this terrific storm of dust, at times one side of the street was quite invisible to the other, shops had to close all doors, and even then a very fine deposit of dust remained on everything after the storm was over, which eased itself down as the sun declined, and was entirely over at sunset. The fine dust seemed to have attained an altitude of from one mile to a mile and a half, and was travelling from about W.N.W. to E.S.E. (no compass here). When over, the roads were swept clean of fine dust, and the coarse sand lay in regular ridges, the same as waves leave it on the sea beach. Perhaps Adelong could give further information, as the storm came from their direction. No doubt the fine dust travelled out to sea until beat down by the rain, for I see by the public prints that you had this storm at Sydney the same night. I enclose some of the fine dust obtained from nooks and corners of elevated places, so that you may compare it with that your Moruya correspondent sent you."—EDWARD ALLEYNE.

"Moruya Heads, Meteorological Station, 22nd Dec., 1880.

"I have forwarded three samples of the mud or dust shower of the 15th instant; the samples have been carefully collected with a very fine brush, and I think contain very little of any other matter than that which fell during the shower; a great deal has been blown away since the 15th, though now all the bushes, leaves, small trees, &c., show it very plainly. On the morning after the shower a few pounds weight could have been collected from tubs, buckets, rain gauge, &c., but it was all thrown away.

"Concerning the shower, no particular notice was taken of it, the drops were large. It had been gloomy all day and threatening, and a low barometer; we had a southerly squall about 6 a.m., which cleared off about 8 o'clock, mizzling rain at 9 and cloudy, wind light southerly, with a smart shower at 10, then light showers until 2 or 3 o'clock the following morning. At 5 a.m., 16th, the weather was fine and clear. We had a quantity of clothes on the grass all night, which were all covered with mud, yet only thought it strange how it came there, until reading about the *Potosi* steamer having been in such a shower. She must have been about 40 miles south of the Moruya heads at the time. I have not heard of it being at any other place than Moruya, and a few miles along the south coast; it looks very much like the rust on wheat."—R. M. TRANENT.

"Yaas, 23rd December, 1880.

"I noticed by Tuesday's *Herald* that you wish to get information about the late dust storm. I am informed by several parties that the storm rose a long way back, most of the dust rising off the stations between the Lachlan and Darling, crossing over Condobolin, Euabalong, and Forbes, about 12 o'clock on Wednesday morning, the 15th. I have been living in the Cobar district many years, and always found the dust very bad in summer, especially in very dry times. A flock of sheep going in to get water at a tank will rise the dust so that it can be seen plainly at a distance of 30 and 40 miles, travelling in the air the same as smoke from a bush fire (and it takes an experienced hand to tell the difference). I may mention the dust passed over Gunning between 5 and 6 o'clock on Wednesday evening, 15th, the wind being from south-west."—C. E. ARMITAGE.

"Wingen, Jan. 23rd, 1884.

"We have had here a rather remarkable appearance in the air. On Sunday morning, January 20th, the thermometer record for the previous 24 hours was 88 max., 53 min., with wind blowing from the west, and that night we had a light thunderstorm, with 41 points of rain. On Monday, the 21st, the thermometer record for previous 24 hours was 98 max., 60 min., and the wind blowing strong from the north-west, and the country was covered all day with a light haze which did not appear at all like smoke nor like ordinary dust. This continued all day, and on Tuesday morning the thermometer record for the previous 24 hours being 84 max., 55 min., the wind blowing strong

all day from the same point, the country was still covered with haze. To-day, Wednesday, the 23rd, the thermometer record for previous 24 hours was 81 max., 57 min., wind blowing from the same point, the haze has quite disappeared. The wind during the whole time seemed cool and moist, which seemed the more remarkable as we have for weeks past been having hot dry winds from the same point. The idea which suggested itself to me was that there had been heavy rain in the north-west, as the feeling in the air and the appearance was much like what sometimes occurs in Sydney when a southerly buster comes up after a very hot day."—W. E. ABBOTT.

"Dust Storm of August 14th, 1885, as seen at Hay.—The night of the 13th August, during the ride in the coach from Gunbar to Hay, was most beautifully clear. At the commencement of the last stage, 20 miles from Hay, at 5 o'clock a.m., August 14th, the wind was blowing pretty freshly from the north. Later on there was a magnificent sunrise, the air being as clear as could be. On reaching Hay about 7.30 a.m., the wind was blowing strongly and increased up to 10 a.m., when it was blowing in heavy gusts from the north. It continued in this way till about 2.30 p.m., when it gradually grew calmer and veered to the south-west. At 7.30 a.m. the barometer stood at 29.396. It fell steadily until 2 p.m., when it commenced to rise. About 10 a.m. the whole place was enveloped in a light reddish-brown fog, which continued all day. The particles of dust composing this fog, if it may be so called, being too fine to be seen, no motion was observed, although the wind was blowing in strong gusts. The day was warm and rather close, the temperature being 70°. A light reddish-brown dust was deposited on everything. The wind got much calmer towards evening, and after sunset a slight shower of rain fell. The morning of the 15th was fine and rather cold. There were a few cirrus clouds, the white back-ground of which showed a slight reddish tinge in the air, which could not be seen against the blue sky. The rain gauge showed about 0.003 rain with a deposit of mud about 0.001."—J. ARTHUR POLLOCK.

"Buckinbong, Narandera, 13th Feb., 1885.

"Narandera and the neighbourhood seem to be about the worst places visited. As far as I can learn, the storm travelled from Hay to Narandera in 1½ hours, and from Narandera to Wagga 1 hour, but the wind on the surface did not I think exceed 20 to 30 miles an hour, nor was there much dust near the ground. The wind in the clouds seemed of a whirl-wind nature, the appearance before darkness came on being very wonderful, the clouds were rolling and rolling over and under one another. You will probably know that the storm struck Narandera about 2.15 p.m., and total darkness lasted for 15 minutes, succeeded a like time by a sky of red so brilliant you could scarce look at it. I may mention the darkness was blacker or more intense by far than the darkest night. I have interviewed many people since, men who have been in the colonies 50 years or more, but they aver they never saw anything like the storm of Friday, February 6th."—B. BLAIR.

"Kymba, August 15th, 1885.

"At 9 a.m. the wind was N.E. moderate, with the sky slightly hazy, and a mild feeling in the air, similar to what would be experienced on a mild summer morning, although the minimum temperature during the night had been 30°. The barometer (an aneroid) registered 28.50, being 0.10 lower than at 9 p.m. the previous night. By noon the haze had gradually thickened, and the wind had veered to N.W., but came in variable gusts, and the barometer had fallen to 28.35. Shortly after noon, the clouds which came in the wake of the wind, which had increased to a gale, assumed a peculiar aspect—a dun or salmon colour, and the surrounding hills became enveloped in a light yellow, foggy haze, which was thought to be rain. At 3 p.m. the barometer registered 28.33, and remained steady till 6 p.m. The gale blew with considerable violence during this time. After sunset rain commenced to fall in showers, with strong gusts of wind, and with the rain a

quantity of mud fell, which bespattered everything. As an instance, iron tubs placed under spouts had one-eighth of an inch of a red deposit at the bottom this morning, and roofs and out-buildings bore traces of the discolouration. Twenty-seven points fell up to 9 o'clock this morning, and the barometer has been gradually rising since, although light showers have fallen at intervals through the day. As a mud or dust storm seems so unseasonable at this time of the year, I have dried a small quantity of it, and enclose in this letter, as it may be useful in your observations on the subject. The country in this immediate neighbourhood is too damp from the effect of the recent showers to furnish any dust. I may state that the altitude of this place above sea level is 1036 feet, according to Mr. Railway Surveyor Jamieson, who kindly informed me some time ago. The highest reading of the aneroid has been 29.36 since I have had it."—R. J. BARR.

"Narandera Argus Office, August 24th, 1885.

"Some time since Mr. Bryce Blair, of Buckinbong Station, near Narandera, requested me to forward to you details of the very severe dust storm which passed over this district on Friday, the 6th of February last. I enclose herewith extracts from the *Argus* of the 7th of February, which of course can only be accepted from a paragraph point of view. My personal experience I give you briefly in narrative form:—'I returned to my office shortly after two o'clock; there was at that time every indication of a heavy dust storm coming from the west; in the course of half an hour the town was enveloped in dense clouds of red sand, that was no more than the usual experience at intervals during the summer, but suddenly there came a black column (like the densest smoke in appearance) which made the place darker than the darkest night I ever experienced; it was, in fact, the first occasion upon which I realised absolute darkness. Many people in speaking of it afterwards assured me that they had, from very fear, to remain where they were when overtaken by this cloud; for myself, I may say that in my office just before the storm, I had moved from the window, and suddenly I was so confused by the intense blackness that I could not possibly tell where the window was placed, and though knowing perfectly well in what part of the room lucifers, &c., were usually kept, I had to grope about for some time before I could secure the means of kindling a light. As a matter of fact, I can say nothing stronger than that it was darkness that could be felt.'—GEO. ELDRIDGE.

"Gundaroo, 30th December, 1885.

"Such an unusual and strange occurrence took place here this morning that I thought I would communicate it to you. About half-past six a.m., on looking out the whole of the hills in the distance, west and south, seemed enveloped in a cloud of dust or fog which gradually rose and worked round south to east. About seven, the hills west were cleared, but the dust hung in mid air like a cloud, excepting at two or three places, where it hung as if the dust was falling like a shower of rain; at about a quarter past seven it had all blown in a body to the south, which was so dense that the hills only a short distance away could not be seen, and then it came blowing down direct north; it then took a north-west direction and died away. Now at a quarter to eight a.m. there is hardly a breath of air, with the sun shining out hot; during my thirty-one years' residence in this part I never saw the like before, and thought such a strange occurrence deserved notice being taken of, and this is my reason for troubling you with the details."—WILLIAM AFFLECK.

(To be continued).

New Publication.—The first number of the *Journal de Chimie Physique* will appear shortly. It will be published in Geneva by M. Philippe A. Guye, Professor of Chemistry at the University of Geneva, and will deal with all matters concerning electro-chemistry, thermo-chemistry, radio-chemistry, mechanical chemistry, and stochiometry, and will contain abstracts of all papers on physical chemistry appearing in other countries, &c.

NOTICES OF BOOKS.

Il Moto dei Ioni nelle Scariche Elettriche. ("The Movement of the Ions in the Electric Discharge"). By AUGUSTO RIGHI. Bologna: Nicola Zanichelli. 1903.

THIS reproduction of a lecture given in March before the Italian Electro-technical Society has been slightly enlarged for publication. Though the author apologises for any defects or deficiencies which might naturally be expected to characterise a lecture delivered under the circumstances spoken of in the preface, it is difficult to see in what respects any improvement could be made in the treatment for the benefit of the general reader, previously unacquainted with this most interesting and important subject, branches of which Prof. Righi is at the present time investigating with the originality and thoroughness which mark his work. The lecture aims at being chiefly historical and descriptive, and speaks more of what conclusions have been actually arrived at than of what is as yet unexplained; thus, while containing nothing new, it is an eminently readable account of recent work, and all interested in the subject will find it a useful introductory sketch. Some debatable statements must necessarily be expressed more or less positively in a sketch of this kind, but it is in all respects very fair and well-balanced.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 25, June 22, 1903.

Preparation of Carbides and Acetylenic Acetylides by the Action of Acetylene Gas on the Hydrides of the Alkalis and Alkaline Earths.—Henri Moissan.—The author finds that at a temperature of 100° the alkaline and alkaline earth hydrides react on acetylene gas, producing acetylenic acetylides, and setting free hydrogen. This reaction is important because it allows of the transition easily, and at a low temperature, of hydrides into carbides. It is enough to heat acetylenic acetylide in a vacuum for dissociation to take place, and the acetylene group to be destroyed and the corresponding carbide produced. This process, therefore, constitutes a new method of preparation of the carbides of the alkalis and alkaline earths. At this temperature of 100°, ethylene and methane do not react on the different alkaline hydrides.

Influence of Solvents on the Rotatory Power of Certain Molecules. Derivatives of Camphor.—A. Haller and J. Minguin.—Benzene always exercises an action on the rotatory power of certain camphor compounds, but the differences are not so marked as in the

case of molecules possessing the complex $\begin{array}{c} \text{C}-\text{R} \\ | \\ \text{CO} \end{array}$.

Estimation of Vanadium in Alloys.—Paul Nicolardot.—The methods actually known for the estimation of vanadium are either very long or not very accurate. The author modifies Sefström's method for the detection of vanadium in iron, to render it capable of a quantitative application. Steels and irons, containing vanadium, when attacked by sulphuric or hydrochloric acid, leave a black residue consisting chiefly of graphite, silica, and a little vanadium. If all chance of oxidation is removed, the vanadium remains behind in the metallic state, no trace of this metal being found either in the dissolving liquid nor in the gaseous products evolved. A perfectly accurate and fairly rapid means of estimating vanadium in alloys may thus be employed.

Etherification of the Hydracids.—A. Villiers.—The etherification of the hydracids presents a certain number of anomalies which can be attributed to two different causes:—(1) The existence of hydrates formed by the hydracids, which can be distinguished from those of sulphuric acid by the dissociation which takes place under the influence of heat; (2) the production of ordinary ether with liberation of water. This production is more abundant the higher the temperature, the contrary taking place with sulphuric acid, in which case the temperature influences the rapidity of the formation of ether and not the final proportion.

Benzoyl-derivatives of Hydrazobenzene.—P. Freundler.—The author prepares monobenzoylhydrazobenzene, $\text{C}_6\text{H}_5-\text{N}-\text{N}-\text{CO}\cdot\text{C}_6\text{H}_5$, by effecting the benzoylation in pyridic solution of hydrazobenzene. He also examines the properties of this substance.

Certain Compounds of Gold Chloride and Pyridine.—Maurice François.—Chloroaurate of pyridine, $\text{C}_5\text{H}_5\text{NHCl}\cdot\text{AuCl}_3$, is only stable in presence of hydrochloric acid and gold chloride. Under the action of hot water it easily yields a compound, $\text{C}_5\text{H}_5\text{N}\cdot\text{AuCl}_3$. There also exists a compound, $(\text{C}_5\text{H}_5\text{N})_2\text{AuCl}_3$, which can be prepared either anhydrous or hydrated. The constant production of the compound $\text{C}_5\text{H}_5\text{N}\cdot\text{AuCl}_3$, as distinguished from the other compounds of pyridine and gold chloride, by the action of water or heat is remarkable.

Phenyl Substitution in Phenylmethanes; their Carbinols and their Chlorides.—Jules Schmidlin.—The author measures the heat evolved or absorbed during the phenomena of substitution, and in particular during the substitution of hydrocarbons amongst themselves, and with hydrogen. The heat of substitution is measured by an indirect method, by which the number is deduced from the difference between the heat of formation of the compounds from their elements, these being themselves calculated from the heats of combustion.

Preparation of Nitrous and Nitric Ethers.—L. Bouveault and A. Wahl.—Nitric ethers can be prepared by the action of nitric acid on alcohols, and concentration in the cold either over sulphuric acid or under reduced pressure. In either case each particular alcohol must have its own conditions of concentration and temperature. Nitrous ethers can be prepared by the action of the vapour of nitrous acid on alcohols.

Chlorine Derivatives of Methylene Chloroacetate and Diacetate.—Marcel Descudé.—Acid chlorides easily combine with polymerised formic aldehyde when in the presence of zinc chloride. During the reaction two groups are formed, $\text{R}-\text{COO}-\text{Cl}$ and $\text{R}-\text{COO}-\text{CH}_2$.

Methylene chloroacetate or monochlorated methyl acetate can be obtained by the direct action of chlorine on methyl acetate. The action of chlorine can be pushed further, chlorated and less well known bodies being obtained, but the substituting action of the chlorine takes place on the CH_3 group directly attached to the oxygen.

Bodies of the Pyranic Series.—R. Fosse and A. Robyn.—In a previous paper one of the authors examined the oxidising power of certain pyryl salts. These exercise a remarkable action on alcohol, oxidising it into aldehyde, and being transformed themselves into pyranes. The authors now further investigate this reaction, not only to establish a generality, but also to obtain new pyranes, of which only a small number have been at present prepared.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 2.

Bipolar Electrodes with an Insoluble Anode.—André Brochet and C. L. Barillet.—The authors have found that in electrolysis with insoluble bipolar electrodes, the flow of the current is affected strongly on account of phenomena of polarisation. The quantity of electricity

traversing the metallic strip is extremely small, while that derived from the liquid is relatively considerable.

Bipolar Electrodes with a Soluble Anode.—André Brochet and C. L. Barillet.—Already noticed.

Remarks on the Use of Bipolar Electrodes.—André Brochet and C. L. Barillet.—As a result of their researches on bipolar electrodes, either with soluble or insoluble anodes, the authors have come to the conclusion that soluble anodes influence the flow of the current in the same manner as insoluble ones. To get the best effects with bipolar electrodes, they should form water-tight compartments; the spaces reserved for circulation should be as narrow as possible to prevent losses by derivation. In an electrolyser metallic pieces may be employed, not communicating with the electrodes, not only if the metal acts as an insoluble anode, but more particularly if it acts as a soluble anode.

Complex Salts of Platinum. Plato-oxalonitrites and Plato-oxalonitrous Acid.—M. Vèzes.—Already inserted in full.

The Polymers of Methanal.—Marcel Descudé.—The commercial product known as trioxymethylene does not answer to the formula $(CH_2O)_3$. The various commercial polyoxymethylenes do not all behave in the same manner with certain compounds, especially with chloride of acetyl. With some, in the presence of chloride of zinc, there is instantaneous and integral union, molecule for molecule, in the cold; with others, under the same conditions, there is a commencement of the reaction, but the greater portion of the polyoxymethylene remains unattacked. The author has made a comparative examination of these different products. He found that their solubility in water is the more easy in proportion as their reactional activity is the more energetic. He thought that this might be due to a different state of physical aggregation, the molecules being less apt to take part in a reaction, or go into solution, as their state of condensation is more advanced. The results obtained by experiment confirmed this opinion. He found, in fact, that the product is more active, more easily soluble in water, and its proportion of carbon is further from 40 per cent as it becomes more volatile. Further, that the small quantity of water it may contain does not seem to play any active part, since it can be completely eliminated in some cases without the properties of the bodies being modified in any manner.

The Variations of the Densities of Hydro-alcoholic Mixtures.—H. Vittenet.—As the densities of mixtures of water and alcohol had not been determined for solutions containing less than 10 grms. of ethylic alcohol per litre, the author has undertaken to fill up this gap. The results obtained are given in the following table, and are sufficiently clear not to require any further comment:—

Proportion of the hydro-alcoholic mixtures.		Weight in grms. of equal volumes of the hydro-alcoholic mixtures.	Densities.
Water.	Alcohol.		
100	0	100.8504	1.
999	0.9977	109.8294	0.99980
998	1.9469	109.8082	0.99961
997	2.9922	109.7860	0.99941
995	4.9865	109.7460	0.99904
993	6.9809	109.7024	0.99865
990	9.9726	109.6388	0.99807

Acetal and its Products of Hydrogenation.—André Kling.—Already noticed.

No. 3.

The Temperature of Inflammation and the Combustion in Oxygen of Three Varieties of Carbon.—Henri Moissan.—Already noticed.

Hydrogen in the Air; its Influence on the Determination of the other Gases, and the Density of Nitrogen.—Armand Gautier.—This paper is to a great

extent a criticism of the opinions expressed by M. Leduc and Lord Rayleigh on the proportion of hydrogen stated by the author to be present in the air.

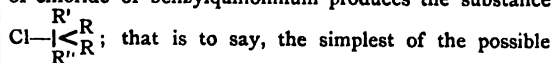
Application of the Theory of Electric Batteries to the Quantitative Separation of Metals.—A. Hollard.—Already inserted in full.

Action of Isocyanate of Phenyl on some Free Oxyacids (IV.).—E. Lambling.—In previous papers the author has described the products of the action of isocyanate of phenyl on the ethers of a certain number of oxyacids. He further examined the action of the carbanile on the same oxyacids in the free state. He now goes on with the examination of the phenylurethane of the anilide obtained with some of the oxyacids used in the course of his research. The experiments described are the action of isocyanate of phenyl on glycolic acid, on lactic acid, on trichlorolactic acid, on α -oxybutyric acid, on α -oxyisobutyric acid, on phenylglycolic acid, and on benzylic acid.

The presence of Volemite in some Primulacæ.—J. Bougault and G. Allard.—Already noticed.

Derivatives of Cyclohexene by Addition.—Leon Brunel.—Already noticed.

The Chloride and the *d*-Camphosulphonate of Benzylquinolinium.—A. Reyckler.—The observations made in this research seem to show that the direct synthesis of chloride of benzylquinolinium produces the substance



constitutions. The chloride of benzylquinolinium, $C_9H_7N.C_7H_7Cl$, was obtained in the following manner:—An equimolecular mixture of chloride of benzyl and quinolein was heated to 100° for a couple of hours in a flask which only communicated with the air through a narrow tube; water and alcohol were also added. A quasi-colourless solution was obtained which, when treated with a large quantity of water and then submitted to several extractions by ether, to remove the remainder of the original products, gave, on evaporation, a well crystallised residue. When purified by re-crystallisation in absolute alcohol, this substance appeared as colourless prisms, very soluble in water, less so in cold alcohol. On drying, to determine the fusion-point, the author observed that at about 130° to 140°, the substance took a rose tint, which increased as the temperature became higher, and melted with considerable swelling at about 170°, forming a deep red liquid. The *d*-camphosulphonate of benzylquinolinium was obtained by reacting in warm alcohol with equimolecular quantities of the preceding chloride and *d*-camphosulphonate of silver. The filtrate, freed from impurities, gave, on evaporation, a quasi-colourless crystalline mass. After purification by re-crystallisation in acetic ether and alcohol, and in the same ether mixed with acetone, a nearly theoretical return was obtained of large, colourless, crystalline plates, fusible at 122°.

The Decantation of Mineral Waters; its Influence on the Chemical Composition and Bacteriological State.—Ed. Bonjean.—Decantation is an operation practised on mineral waters which cannot be kept in bottles in a sufficiently limpid condition; these are principally ferruginous water. Decantation is accompanied by a production of nitrites, but this phenomenon is fugitive. From the bacteriological point of view, decantation is very objectionable. On leaving the ground a sample of Apollinaris water was sterile.

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" 6 " "	649
And when leaving the reservoir for bottling	116

MISCELLANEOUS.

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—*Examination in Biological Chemistry.*—The Council have resolved that the Examination in Biological Chemistry, hitherto a Branch of the Final Examination for the Associateship, shall in future be open to Fellows and Associates of the Institute who desire to obtain testimony of their knowledge in this branch of work. The Examination, while suited to those intending to practise their profession in its relation to the chemistry and bacteriology of water, sewage, and effluents, can also be taken by those who are interested in the chemistry of Brewing, and other industries involving both chemical and bacteriological knowledge, and by pathological chemists.

The Final Examination for the Associateship in the Branch of Biological Chemistry.—An Examination in the Branch of Biological Chemistry will be held at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., on Tuesday, October 20, 1903, and three following days. The Examination is open to any Candidate whose application for admission to the Final Examination has been accepted by the Council, and to any Candidate who has passed the Intermediate Examination of the Institute. Candidates desirous of presenting themselves are required to notify the Registrar on or before Tuesday, September 15, 1903, when the list of Candidates for this Examination will be closed. The Examination will extend over four days, and may be theoretical, practical, written, and oral, and the syllabus will include the following:—Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and the practical applications of Biological Chemistry to Industries. Candidates presenting themselves in any Branch of the Final Examination are expected to possess a general knowledge of all branches of Chemistry in addition to a thorough knowledge of the particular Branch of Chemistry selected. The Examiners are at liberty to apply any test they think desirable, either *visu voce*, or by writing, or by experimental work, in order to obtain evidence as to the practical knowledge of Chemistry possessed by the Candidate. Candidates must be familiar with the use of such scientific instruments as are commonly found in chemical laboratories. Any Candidate for the Final Examination may present a thesis upon any chemical subject to which he has paid special attention; and the thesis, if approved by the Examiners, may be taken as part of the Examination. Candidates are also at liberty to submit note-books containing records of any work done by them which have not already been inspected by the Examiners. The contents of note-books will be taken into consideration.

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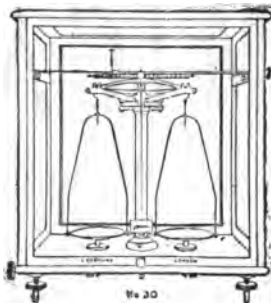
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SEPARATION OF SOLIDS IN THE SURFACE-LAYERS OF SOLUTIONS AND "SUSPENSIONS."*

OBSERVATIONS ON SURFACE-MEMBRANES, BUBBLES,
EMULSIONS, AND MECHANICAL COAGULATION.

(PRELIMINARY ACCOUNT).

By W. RAMSDEN, M.A., M.D., Oxon.,
Fellow of Pembroke College, Oxford.

In a paper published in Du Bois Reymond's *Archiv. für Anatomie und Physiologie*, in 1894 ("Physiologische Abtheilung," pp. 517-534), I showed that mere agitation of various proteid solutions brought about a separation of some of their contained proteid in the form of fibrous or membrano-fibrous solids, and that it was possible in this way to coagulate and remove the whole of the proteid from solutions of egg-albumin. It was proved also that these de-solutions and coagulations of proteid were not due to the action of enzymes, heat, or surface evaporation, and were not appreciably affected by the nature of the gas in contact with the liquid, or of the vessel in which the agitation was effected.

A prolonged series of further experiments, undertaken with a view of ascertaining the precise cause of this phenomenon, has led me to the discovery of an important, but hitherto unnoticed physical fact—namely, that, quite apart from evaporation, solid or highly viscous coatings are spontaneously, and more or less rapidly, formed on the free surfaces of all proteid solutions.

By purely mechanical means these free-surface coatings can be heaped up to form visible solid masses of proteid, which in some cases is not only "de-soluted," but at the same time coagulated and rendered permanently insoluble in the mother-liquid.

By extending the range of my experiments, I have been led to the further conclusion that similar coatings of solid or highly viscous matter occur on the free surfaces of a large number of non-proteid colloid solutions, of fine and coarse "suspensions," and of a few apparently crystalloid solutions, and that they are formed also at the interfaces of every pair of liquids which, without being of high viscosity, are capable of forming persistent emulsions.

The explanation of these spontaneous de-solutions of previously dissolved matter at the free surfaces must be sought in the observation, which I have found to hold good in all cases hitherto examined, that the matter which accumulates possesses the property of lowering the surface-tension, and, therefore, the "surface energy," of the free surface of water.

On dynamical grounds, the most stable arrangement of any solution, taking surface-tension considerations only into account, must be one accompanied by minimal "surface energy." A dissolved substance, if it increases the potential energy of a surface, will tend to leave that surface, or if it diminishes it, to accumulate at that surface. This principle has been recognised as holding good in crystalloid solutions (*vide* J. J. Thomson, "Application of Dynamics to Physics and Chemistry," p. 251), but has not hitherto been shown to apply to colloid solutions and coarse "suspensions."

The same considerations may be applied in explanation of the accumulations observed at the interfaces of liquids forming persistent emulsions.

The formation of surface pellicles, the separation of various solids by mechanical treatment adapted to produce heaping up of surface-films, the power of forming moderately persistent bubbles possessed by various lipid solutions, and the power of forming persistent emulsions possessed by various immiscible liquids, are all explained (in the numerous cases where there is no evidence of chemical change) as due to diminution of the surface-energy brought about by accumulation of certain dissolved or suspended matters at the surfaces concerned, and to the physical properties of the accumulated material.

It is remarkable that the very common occurrence of these free-surface accumulations has hitherto escaped general notice. Doubtless this is due to the extreme delicacy and fragility of the solid coating, and to its generally rapid re-solution, when by contraction of the surface it is heaped up in local excess, or when by the substitution of some other surface, the reason for such accumulation has been removed. For the production of visible masses of solid, or of deformed angular bubbles, it is in fact necessary that the surface-solid shall either be rendered insoluble by the mechanical treatment to which it is subjected, or shall be heaped up more rapidly than it is re-dissolved.

Full details of the methods employed, the control experiments made, and the results obtained, together with references to the work of others in the same field, I hope to publish shortly. Meanwhile, a brief summary of the main points will be found in the following observations:—

1. The presence of a free (*i.e.* gas) surface is essential for the production of the de-solutions and coagulations described in my previous paper.
2. By simple and gentle mechanical means adapted to produce heaping up of the surface-films, large masses of solid ("mechanical surface aggregates") can be separated out from all proteid solutions, and from a large number of colloid solutions and suspensions (*vide* table at end of paper). In the three cases where the dilution-limit has been ascertained, solid "mechanical surface aggregates" have been obtained from liquids containing as little as one part of dissolved or suspended solid in 1,000,000 parts of water.
3. The separated solids differ greatly from one another in the rapidity and completeness of their re-solubility in the mother liquid, and they are sometimes insoluble and "coagulated."
4. They may have a delicate membranous, membrano-fibrous, or fibrous structure, simulating that of various biological tissues, or they may consist of particles lying loosely side by side (*e.g.*, sulphur).
5. The film of the free surface of all proteid solutions, and many of the various solutions or suspensions which yield solid "mechanical surface aggregates," exhibits a specially high viscosity, not met with in the bulk of the solution. This "special superficial viscosity" develops at very different rates in different solutions, and attains very different degrees of maximal intensity. In some solutions (*e.g.*, egg-albumin, saponin) it develops with great rapidity; in others (*e.g.*, serum-albumin, methyl-orange, ferric acetate, mastic, &c.) several minutes, or even hours, may be necessary for any considerable development. Evaporation hastens its development, but is not essential. Slight convection currents have a powerful accelerating influence, but are essential only when the suspended solid is indiffusible. The nature of the gas in contact with the "solution" is a matter of indifference, provided it be chemically inactive.
6. In most cases the "special superficial viscosity" is accompanied by a special superficial resistance to "shear." This is often so intense that a magnetised needle floating on the solution is capable of rotating the vessel containing the solution, if this be floated on water or suspended by a fine thread, and the needle be exposed to the attraction of a magnet.
7. The presence on a liquid of a thin coating of matter (even of liquid) which diminishes the "surface energy"

* A Paper read before the Royal Society, June 18, 1903.

would account for some "special superficial viscosity" (Marangoni), but would not account for superficial resistance to "shear," unless the coating of matter were solid or highly viscous and also coherent.

8. Bubbles of solutions of egg-albumin, caseinogen, and saponin exhibit remarkable phenomena, which show that the bubble-film as a whole is very imperfectly elastic, and is covered with solid membranes. Egg-albumin bubbles are deformed on collapse by the formation of persistent folds of solid proteid in the bubble-film. Bubbles of pure saponin solution, containing 0.01 per cent or more of saponin, fall on collapse into innumerable shimmering folds containing isolated curved rods of solid saponin, although water is capable of dissolving at least 2500 times this amount.

The collapsing bubble assumes extraordinary shapes, with sharp angles (as observed by Plateau), and when a hanging bubble is broken, a ragged curtain of bubble-film, which instantly becomes dull and opalescent, hangs for some five or ten seconds from the edge of the supporting tube.

9. The presence of such solid membranes on a bubble must contribute greatly to its persistence. Further, the mere presence of solid particles on the surfaces of a bubble has, in many cases, been found to add greatly to its persistence, even when, judging by the absence of a special resistance to shear in the film of a free surface of the solution, such particles are not appreciably coherent, but lie loosely side by side (e.g., in suspensions of sulphur, picric acid, quinine bisulphate, salicylic acid).

In the cases quoted, a bubble of air can be seen to pick up the particles in suspension as it passes through the liquid, and to retain them obstinately when it reaches the surface and comes to rest, so that the bubble becomes thickly coated with solid particles, although the liquid contained only a small quantity of suspended solid, and this solid is specifically heavier than the solution.

10. Every solution capable of forming moderately persistent bubbles, which has hitherto been examined, has yielded solid or highly viscous mechanical surface aggregates. This very remarkable fact indicates that the power of forming such bubbles is due to the presence of matter which has accumulated at the free surfaces in a solid or highly viscous condition. The cohesion of the matter, so as to form an appreciably coherent membrane, is apparently not essential, but it occurs in most cases where the bubble is very persistent.

Plateau recognised this association of the power of forming persistent bubbles with a special superficial viscosity and a diminished surface-tension, but did not connect these phenomena with the formation of a coating of matter derived from the solution, and specially concentrated at a free surface (*vide* "Statique des liquids," pp. 69-71).

On theoretical grounds, the presence of a thin film of liquid, even of low viscosity, on the free surfaces, should also be capable of increasing the persistence of a bubble if the liquid be such as diminishes the surface energy of the mother solution, but increased persistence brought about in this way appears to be very slight compared with that occurring when the coating consists of solid or highly viscous particles.

11. The effects which the presence of solid particles in the surface layer exercises upon the persistence, size, and other properties of bubbles, depend on many factors. Many solutions in which surface accumulation of solid undoubtedly takes place have been found incapable of forming large or persistent bubbles. The size of the particles, their surface tension relations, the rate of their accumulation, the rate of their resolution when forced by mechanical means into local excess, and the elasticities and flexibility of any membrane formed, are all concerned in conferring on different bubbles the marked individuality which characterises them, and in making the formation of large or persistent bubbles possible. Solid particles, which diminish the surface energy of the free surface, may be regarded as adding in three ways to the persistence of a bubble:—

- i. By serving as *points d'appui* (*cf.* Frankenheim, "Die Lehre von der Cohäsion," Breslau, 1835).
- ii. By actual contact, friction, or cohesion of the particles, opposing local disturbances of the film.
- iii. By opposing such de-formation of the surface as tends to expose a new surface with higher surface-tension (*i.e.*, like oil on water, by the effect of the surface coating in diminishing the superficial energy).

12. It has been demonstrated that an actual solid membrane forms around the globules of several persistent emulsions, and at the contact interfaces of several pairs of liquids capable of forming persistent emulsions (e.g., pure neutral olive oil and saponin solutions).

The membrane manifests itself by producing the following phenomena:—

- i. Intense viscosity peculiar to the interface, absent at the interface of pure water and the other liquid, and developing only when an emulsifying substance is added to one or other of the liquids.
- ii. Persistently deformed sharply angular and grotesque shapes of the emulsified globules.
- iii. Folds of semi-opaque membrane when the surface of separation is subjected to appropriate de-formation.

Such direct optical evidence of the presence of a constraining membrane separating liquids which form persistent emulsions is exceptional or, if it occur, is usually fugitive (*cf.* air-bubbles). An intense "special interface viscosity," pointing to the presence of solid or highly viscous matter, has, however, been found with every pair of liquids capable of forming persistent emulsions hitherto examined.

13. The persistence of many emulsions is therefore determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids. Direct measurements of the various surface tensions concerned are not available, but the close resemblance of the phenomena to those occurring at a free surface, points to the view that accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the "surface-energy" is thereby diminished.

14. Numerous precipitations of colloids from their solutions by chloroform, ether, carbon bisulphide, and amyl-alcohol, are attended by precisely similar phenomena at the interfaces of the liquids concerned, and appear to be brought about in exactly the same way.

15. The suggestion that the observed surface accumulations must be attributed to the diminution of the "superficial energy" thereby produced, is strongly supported by a series of experiments made with watery solutions containing equal quantities of two substances each of which by itself forms "mechanical surface aggregates." In such mixtures there has invariably been preferential accumulation of one substance to the more or less complete exclusion of the other from the mechanical surface aggregate obtained. Thus—

Saponin	➤	Egg-albumin.
Bile-salts	➤	Saponin.
"	➤	Soap.
"	➤	Gamboge.
"	➤	Egg-albumin.
"	➤	Sulphur.
Egg-albumin	➤	Carmine.

If the dissolved substances thus mixed exert no chemical action upon each other, such preferential accumulation is not only explicable, but, taking only surface-tension considerations into account, is theoretically essential when one substance produces a greater diminution of the surface energy than the other. In actual practice, however, the phenomena are complicated by differences in diffusibility and rate of resolution, and by limitation of independent mobility of the "dissolved" particles due to their mutual cohesions and adhesions.

16. It has been found also that bubbles blown from mixed solutions of two substances, each of which by itself forms bubbles presenting recognisable and well-marked

differences of character, behave precisely as if they have been blown from a solution of one of these substances only, and this is always the one which in a mechanical surface aggregate made from the mixed solution is found to have more or less completely excluded the other, *e.g.* :—

Saponin	>	Egg-albumin.
Bile-salts	>	Saponin.
"	>	Egg-albumin.
Egg-albumin	>	Carmine.

17. The fact that the introduction of alcohol (and of other liquids of low surface-tension) into many solutions which show the above described surface phenomena, frequently deprives those solutions of their superficial viscosity and of their power of forming bubbles or of yielding mechanical surface aggregates, would seem to be explicable by similar considerations, *i.e.*, as due to preferential accumulation of alcohol to the exclusion of the suspended or dissolved solid.

18. Various hitherto obscure phenomena find their explanation in the facts observed, *e.g.* :—

- i. The ready formation of a "skin" on hot milk exposed to evaporation is explained by (a) the presence of a delicate skin or pellicle on the free surface even of cold milk or of caseinogen solutions not exposed to evaporation; (b) the presence of a similar pellicle at the inter-faces between caseinogen solutions and pure neutral olive oil or butter-fat.

The existence of a proteid "haptogen-membrane" around the cream-globules of milk cannot any longer be doubted, and their rôle in contributing to the ready formation of a thick skin on hot milk, as first demonstrated by Hertz and Jamison (*vide Journ. of Physiol.*, London, 1901, vol. xxvii., p. 26), finds a complete explanation. The apparently contradictory observations of Rettger (*vide Amer. Journ. of Physiol.*, May, 1902), demonstrating the possibility of obtaining very delicate skins by heating caseinogen and other solutions, although free from fat globules, appear to be due to the dehydration and thickening by evaporation of the surface pellicles present on such solutions even in the cold.

- ii. The homogeneous "Grenz-membran" described by Bütschli (and the optical homogeneity of thin films referred to by Hardy) in various coagulated or dehydrated colloids, is the above described membrane of solid colloid formed at an air or other appropriate surface.

- iii. The high pressure required to force solutions of saponin and albumin through capillary tubes when bubbles of air are present is largely due, among other factors, to the presence of solid membranes around the air-bubbles, and the increased resistance to deformation brought about. As Plateau showed, the resistance offered is enormously greater than that of water containing similar air-bubbles. (*Cf.* air-embolism in the blood-capillaries of a mammal).

- iv. The failure of proteids and other colloids in solution to pass through fine filters without considerable loss is largely due to the formation of surface membranes and mechanical coagula upon air, grease, or other suitable surfaces in the pores of the filter.

19. The following table indicates some of the substances whose aqueous solutions or suspensions have shown evidence of the accumulation of solid or highly viscous matter on their free surfaces, either by (1) yielding "mechanical surface aggregates"; (2) intense special superficial viscosity; or (3) forming persistent bubbles.

It will be seen that there is a very considerable parallelism in the three phenomena. Exact parallelism could not be expected, since the different physical properties of the surface accumulations must necessarily affect the phenomena in different and highly complex ways. Special superficial viscosity has only been recorded when very intense, and all minor degrees have been ignored, since the presence of dust, &c., in minute quantity may, as has been

shown by Lord Rayleigh (*Roy. Soc. Proc.*, 1890, vol. xlviii., pp. 127—140), produce some "superficial viscosity," and it has been practically impossible entirely to exclude such contamination. Power to form persistent bubbles has been shown by either :—

- i. The possibility of blowing 2-inch bubbles.
- ii. The formation of a froth.
- iii. The formation of small bubbles which last in closed vessels at least thirty minutes.

In all cases the substances employed have been of the greatest attainable purity, the de-soluted solids have been shown to consist of the same material as that in solution or suspension, and numerous control experiments have been made.

Aqueous solutions or "suspensions" of—	Solid mechanical surface aggregates.	Intense superficial viscosity.	Persistent bubbles.
Proteids of egg-white—			
1 in 10 to 1 in 100,000	+	+	+
1 in 1,000,000	+	—	—
1 in 10,000,000	—	—	—
Crystalline egg albumin ..	+	+	+
Serum proteids	+	+	+
Serum albumin	+	+	+
Fibrinogen	+	+	+
Alkali albumin	+	+	+
Acid albumin	+	+	+
Caseinogen in clear solution in Na ₂ CO ₃ solution	+	+	+
Gelatin	+	+	+
Primary albumose	+	+	+
Secondary albumose	+	+	+
Peptone (from peptic digestions) soluble in absolute alcohol	+	+	+
Muscle proteids	+	+	+
Plant vitellin from lentil seeds	+	+	+
Sodium palmitate	+	+	+
Sodium oleate	+	+	+
Methyl-orange	+	+	+
Orange G	+	+	+
Spiller's purple	+	+	+
Saponin—			
1 in 100 to 1 in 100,000	+	+	+
1 in 1,000,000	+	+	—
1 in 10,000,000	—	—	—
Sapogenin	+	+	+
Digitalin	+	—	+
Ferric acetate	+	+	+
Cupric acetate	+	+	+
Colloidal ferric hydrate ..	+	+	+
Carmine	+	—	+
Colloidal sulphur	+	—	+
Bile-resin (dysylsin)	+	—	+
Bile salts	+	+	+
"Caramel"	+	+	+
Gum mastic	+	+	+
Shellac	+	+	+
Starch mucilage (½%) ..	+	—	—
Gamboge, 1 in 1000	+	—	+
Gamboge, 1 in 1,000,000 ..	+	—	—
"Flowers of sulphur" ..	+	—	+
Animal charcoal	+	—	+
Quinine bisulphate (solution)	—	—	—
Quinine bisulphate (excess in suspension)	+	—	+
Quinine solution	+	—	+
Picric acid (solution) ..	—	—	—
Picric acid (excess in suspension)	+	—	+
Salicylic acid (solution) ..	—	—	—
Salicylic acid (excess in suspension)	+	—	+

ON THE RADIO-ACTIVE EMANATION IN THE
ATMOSPHERIC AIR.*

By J. ELSTER and H. GEITEL.

(Concluded from p. 32).

II.

ON THE DEPENDENCE OF THE RADIO-ACTIVITY OF THE FREE
ATMOSPHERE ON THE METEOROLOGICAL ELEMENTS.

By J. ELSTER.

FROM December 15, 1901, to the end of December, 1902, we have determined on 155 days altogether the radio-activity of the air at our dwelling place by the method specified by us and already accurately described (*Physikal. Zeit.*, 1902, iii., p. 305). In this method, the metal wire 10 m. long and about 1 m.m. thick, was freely stretched, with ebonite insulators and sodium drying, at a height of about 2 m. above the ground, from one corner of the house to another at right angles to it; a short moistened string connected it with the inner coating of a Leyden jar; the constancy of the charge of the wire was controlled by means of a high-tension electroscope connected to it; the time of exposure amounted always to two hours. It was, however, not always possible for us to watch continually the arrangements for charging the Leyden jar (inductor, water influence machine, high-tension dry pile), but care was taken that the potential of the stretched wire did not exceed 2800 volts, and did not fall below 2000 volts.

Some uncertainty was attached to the numbers obtained by us, for the reason, which became specially obvious later, that the induced radio-activity is more dependent upon the potential of the wire during the exposure than we believed originally. The theory then put forward by us (*cf.* the record of last year's session), that for thin wires the induced radio-activity is practically independent of the potential of the wire while it is being rendered active in free air, so long as this exceeds 2000 volts, can probably not be maintained without limitations, according to more recent developments. In future measurements it will be better to aim at charging the wire to exactly the same potential from day to day than at working with perfectly constant potentials while the activity is being excited in the wire.

After the activity had been excited, the wire was wound on a cylinder of metal gauze, which was introduced (fitting closely to the wall) into the protecting cylinder of our leakage electrometer—closed for this purpose underneath also, except for a central opening. As before, we put the activity of the air = 1, if, after two hours' exposure, a metre of the wire which was rendered active lowered the potential of the leakage substance by 1 volt in one hour. Before each measurement we determined the loss of tension which the leakage substance charged to a potential of about 260 volts experienced in the course of an hour in the closed protecting cylinder by the natural ionisation of the air, and then took this amount into account in the final measurement. To show the method of observation and calculation employed, we give here the record of one of these determinations:—

Excitation of Activity on June 27, 1902.—Cloudiness, 1; high transparency of the air; leakage of electricity, 1.6 per cent; barometer, 763.6; temperature, 26.6° C.; direction and strength of wind. N.E.; wire of 1—3 p exposed with the high tension dry pile; potential of the wire, 2500 volts.

I. Control Experiment, before the Wire is rendered Active.

Initial potential... .. 20.2; scale div. = 264 volts.
Potential after 15 minutes. 19.9; " = 255 "

Loss of tension of leakage substance in fifteen minutes
= 9 volts, thus in one hour = 36 volts.

II. Experiment after Wire is rendered Active.

Initial potential... .. 22.0; scale div. = 264 volts.
Potential after 10 minutes. 10.2; " = 201 "

* Aus der Denkschrift der Kommission für luftelektrische Forschungen, München, 1903.

Loss of tension of leakage substance in ten minutes = 63 volts, thus in one hour = 378 volts.

Effect of wire 10 m. long alone = 378—36 volts = 342 volts.

Effect per metre = $\frac{342}{10}$ = 34.2 volts. Thus A = 34.2 volts.

The meteorological data we took from the information given by the Meteorological Station at Brunswick, the director of which, Herr Klage, most kindly placed them at our disposal.

When specially high or low values of these activity numbers (A) were found, they were often checked many times in the course of the day, and we consider them accurate enough to be used for deducing definite results from the total material accumulated, and hope that thus we shall lead to a repetition of our experiments in other places.

We give here the tables of the means for the months, A (mean), adding the maxima and minima observed, A (max.) and A (min.), as well as the number of days, n, on which observations were taken.

TABLE I.

Months ...	1901.												1902.											
	xii.	i.	ii.	iii.	iv.	v.	vi.	vii.	viii.	ix.	x.	xi.	xii.	i.	ii.	iii.	iv.	v.	vi.	vii.	viii.	ix.	x.	xi.
A (mean) ..	28	14	13	20	16	24	32	—	15	16	9	22	22	50	47	40	40	32	44	64	—	40	32	18
A (max.) ..	50	47	40	40	32	44	64	—	40	32	18	31	34	17	4	5	9	6	18	—	6	5	4	17
A (min.) ..	17	4	5	5	9	6	18	—	6	5	4	4	17	16	20	19	11	13	10	11	—	18	13	11
n ..	16	20	19	11	13	10	11	—	18	13	11	8	5											

Remarks.—The observations are not given for the month of July, nor for days with plentiful atmospheric deposition.

It may be at once concluded from this table that the amount of radio-active emanation contained in the free atmosphere is subject to remarkably great variations. The extreme values are to one another as 16 to 1 (absolute max. = 64; absolute min. = 4). The mean value for the year is 18.6.

To decide the question whether the number of free ions present in the air and their mobility have any influence on the magnitude of the activity number, we have also determined the percentage leakage of electricity, *a*, on ninety-six days altogether, and used the latter as a standard for both quantities. We then divided the coefficients of leakage obtained into nine groups, and associated with the mean of each group of the *a* the mean of the A belonging to it. Thus we got Table II.

TABLE II.—Dependence of the Radio-activity of the Air on
the Leakage of Electricity.

Group No. ...	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
No. of observ. ...	12.	14.	19.	9.	11.	10.	9.	9.	3.
<i>a</i> (per cent)	0.80	1.1	1.4	1.6	1.7	1.9	2.1	2.4	3.3
A (mean) ..	17.1	14.5	16.1	18.1	14.0	17.4	17.7	28.7	29.7
A (max.) ..	40	43	41	32	22	40	64	47	40
A (min.) ..	5	6	5	7	8	5	6	11	21

We were surprised to find that, as shown by this table, for a percentage leakage of 0.8 to 2 the mean values of A differed by only a few units, while the maxima and minima seem to be irregularly distributed through Groups I. to VII. A considerable rise in the values A (mean) and A (min.), compared with the previous numbers, first appeared in the last two groups, unfortunately containing only a few observations.

Against the existence of a direct connection between the radio-activity of the air and the coefficients of leakage may be adduced the fact that the greatest amounts of activity are excited during fogs; the values then obtained exceed or closely approximate to the mean for the year, while the leakage of electricity is known to be small when the air is misty. In Table III. some observations relating to the activity excited in foggy air are collected.

TABLE III.—Radio-activity of the Air in Fogs.

Date.	A.	Remarks.
20/XII./01	25	Wet fog.
23/XII./01	27	" "
13/II./02	41	Light ground fog.
1/III./02	22	Damp fog.
15/XI./02	31	Thick mist.
15/XII./02	16	Fog; hoar-frost.
22/I./03	45	Thick ground fog.

On five days, not included in the table, the activity numbers lay between 4 and 12; thus the foggy air was never inactive. In any case it follows from these observations that the conditions in free air are much more complicated than in closed subterranean spaces, in which the conductivity of the air is closely connected with the amount of radio-active emanation.

The temperature of the air also appears to have a decided influence on its radio-activity. If the values of A are grouped together for temperatures above 0° and below 0°, the mean value of A for 136 observations at temperatures above 0° is 18, and for 19 observations at temperatures below 0° A = 26. Rutherford, also, on repeating our experiments in Canada, found that on cold frosty days the activity of the air is specially high.

As regards the direction of the wind, we found that with winds blowing from the continent, the values of A are on an average higher than with those which blow from the sea. (Cf. Table IV.)

TABLE IV.—Dependence of the Radio-activity of the Air on the Direction of the Wind.

Wind directly from—	A (mean).	A (max.).	A (min.).	n.
S.	22	50	6	14
N.	15	23	4	4
E.	22	64	6	18
W.	12	32	5	23

The remarkably high and often quite irregularly occurring maxima of A were observed mostly with purely southerly or easterly winds, or with those winds which had a southerly or easterly component.

Whether the above theory as regards the direction of the wind always holds good must be ascertained from further experiments, and by using a wire which is exposed at a place where it is equally accessible to winds from all directions, which was not possible for us. The house protected it from currents of air coming directly from the north and east.

For this reason the influence of the strength of the wind is very difficult to ascertain from the materials collected by us. Moreover, out of the 155 observations made, 111 were made when the wind strengths were 4, 5, and 6. Fourteen observations only were made when the strengths were 1 and 2, for which the mean value is A = 23, while for the 9 observations with strengths 7 and 8 A (mean) is 13.5. These numbers appear to show that the activity is higher the more stagnant the air is over the earth's surface. The large values of A found for misty air point to the same conclusion, for at our place of residence fog is almost always associated with complete lack of wind. But it is also quite possible that an optimum of air movement exists.

The radio-activity of the air undoubtedly depends on the height of the barometer (cf. Table V.).

TABLE V.—Dependence of the Radio-activity of the Air on the Height of the Barometer.

Mean bar. height	740 m.m.	750 m.m.	760 m.m.	770 m.m.
A (mean)	23	19	17	13
Number, n	23	56	68	8

This influence of the height of the barometer becomes intelligible when it is remembered that we discovered that the amount of radio-active emanation in that part of the atmosphere which is beneath the earth's surface is

abnormally high as compared with that of the air above the earth's surface. A lowering of the atmospheric pressure must thus cause the air of the ground to be drawn up from the capillaries of the earth into the atmosphere, and hence the activity is increased. So long as the penetrability of the earth's surface is not altered, we must expect that every decrease of atmospheric pressure will be accompanied by an increase of the radio-activity in the free atmosphere. But this is not always the case. If at the same time events occur by which the penetrability of the capillaries of the earth is affected, as, for example, alterations in the position of the underground water, or such changes as partly withdraw from the air the radio-active emanation present in it, e.g., abundant precipitation,* a rise of activity must not be expected with a falling barometer.

To prove these results which naturally follow from the radio-activity of the air of the ground, we resumed the experiments from February 14th to March 29th of this year, taking a measurement daily.

In Table VI., $-\delta B$ denotes the fall of the barometer; $\pm \delta A$ the increase or decrease observed at the same time in the activity number. In the given period, a steady fall of the barometer in the course of two or more successive days took place fourteen times. On looking at the table we see that if we except some anomalies observed after the fall of dust, which was known to occur on February 22nd, in ten cases with decreasing atmospheric pressure, an increase of radio-activity occurred, and only in four cases the alteration in the value of A took place in the opposite direction. In these measurements, in order to shorten the time of observation, the wire which was to be rendered active was only exposed for thirty minutes; for which reason for the given period of time the differences between A (max.) and A (min.) are much smaller than if the exposure had lasted two hours. The values of A now ranged from 4 to 24 as compared with 4 and 64 in the earlier measurements.

TABLE VI.—Summary of the Increase of Activity with Falling Barometer.

Interval.	$-\delta B$.	δA .	Remarks.
From— To—			
18/II. 23/II.	-13.5	+14.6	On the 22nd a transitory alteration in the opposite direction, after fall of dust and rain.
24/II. 25/II.	-1.5	+4.8	
25/II. 26/II.	-4.7	-13.8	Alteration in the opposite direction. On 26th, 7 o'clock a.m., it was raining; the second day was rainy.
26/II. 28/II.	-10.7	+12.7	
1/III. 3/III.	-19.9	+3.0	
4/III. 5/III.	-0.6	+3.9	
9/III. 10/III.	-5.0	-8.1	Alteration in the opposite direction.
10/III. 11/III.	-0.4	+6.9	
14/III. 15/III.	-3.7	+5.4	
15/III. 16/III.	-3.9	-6.7	Alteration in the opposite direction.
17/III. 18/III.	-6.2	+6.8	
21/III. 23/III.	-7.8	+10.1	
23/III. 24/III.	-1.3	-19.7	Alteration in the opposite direction, after a heavy fall of rain at night.
25/III. 27/III.	-6.8	+13.5	

In the course of the month of July, 1902, we performed activity experiments at other places; Geitel in the first half of the month at Clausthal in the Hartz, and in the second half on the shore at Zinnowitz on the Baltic Sea, while

* According to C. T. R. Wilson's and McLennan's researches, rain and snow are active by induction. Thus the suggestion here made; probable (cf. J. C. McLennan, "University of Toronto Studies Physical Science," Series 1903, No. 1, p. 12).

Elster performed similar experiments from July 6th to 31st on the north Frisian Island, Juist.

Geitel's results, as far as they extended to experiments with the air of cellars, have already been given in the preceding part of this communication.

For the experiments in Juist we used the portable apparatus arranged by us for the determination of the radio-activity of the air (*Physikal. Zeit.*, 1902, iv., No. 4, p. 2), consisting of the leakage electrometer, the high-tension electroscope, the high tension dry pile of about 2500 volts, and two bell-shaped wire-holders with ebonite insulators, and sodium drying. This apparatus, we might mention, has proved quite trustworthy throughout, even in damp weather, and with the air filled with salt dust, we could charge the wire system a short time after connecting to the negative pole of the pile, so that the high tension electroscope showed 2200 volts, and little sparks could be drawn from the wire.

The measurements were not taken on the beach itself, but at an open space in the village. The wires were insulated, and stretched between two bamboo rods at a height of about 3 m. above the earth's surface. From the stretched wire a conductor led at right angles to the negative pole of the pile, which in hot weather stood on a little table in the open air in the sun; in unsettled weather, on the other hand, it was placed in a house; in this case the wire was led in through the open window.

Measurements were taken on twenty-one days altogether. The mean value was A (mean) = 5.2; the maximum, A (max.) = 15.8, was observed during a N.N.W. storm and squally weather on 11/VII.; the minimum, A (min.) = 1.6 on 25/VII. when the wind was light S.W. and the sky cloudy.

If we compare with these the values obtained in Wolfenbüttel from June 20th to July 1st, and again from August 1st to September 1st under exactly the same experimental conditions (in these periods of time the high tension dry pile was exclusively used) :-

June : A (mean) = 27, A (max.) = 34, A (min.) = 16;
 $n = 5$.
 August : A (mean) = 15, A (max.) = 40, A (min.) = 6;
 $n = 18$.

We must conclude that the sea air contains only about one-third as much active emanation as the air of Wolfenbüttel. Nevertheless, the leakage of electricity was certainly not less than with us. The mean of 21 (double) observations was $a + = 1.23$, $a - = 1.89$; thus a (mean) = 1.56 as against 1.43 in Wolfenbüttel in June and 1.35 in August (*Wien. Bed.*, 1902, vol. iii., II. A., p. 961); thus the mean percentage leakage in July with us may be given very approximately as 1.4.

This circumstance that the sea air conducts as least as well as, but nevertheless contains less radio-active emanation than the air over the interior, certainly points to the fact that other sources of the ionisation of the atmosphere exist than the penetration of the air of the ground. The few observations which Geitel took at Zinnowitz on the Baltic Sea led likewise to lower activity numbers for the free air than in Wolfenbüttel; a measurement in Clausthal gave $A = 33$.

The small radio-activity of the air over Juist shows also that activities excited by the natural electric field of the earth are far less decided than with us. In a stiff sea breeze it is easily possible to hold a kite for hours at a very considerable height above the earth's surface. Such experiments were carried out many times on days with an electric fall of 200 to 400 volt/meter, which often occur in Juist. The activity of the upper end of the kite string was, however, very small. On 5/VII. A was 1.6; on 8/VII., $A = 2$; on 19/VII. A was only 0.4; and on 22/VII. A was 2.3. On using a string moistened with seawater on 27/VII. A was 3.7. These values are of the same order of magnitude as those obtained with earthed wires stretched horizontally at about 10 m. above the surface, with a fall of potential of about 100 volt/meters (cf. our last year's report).

ON THE

MANUFACTURE OF SULPHATE OF COPPER.*

By GUSTAVE GIN.

THE usual method adopted for the manufacture of sulphate of copper depends on the direct attack of copper or binocide of copper by sulphuric acid.

This method is good when the production of sulphate of copper is simply the consequence of other metallurgical operations of greater importance; for example, in the separation of the precious metals alloyed with the copper.

In such cases, the cementation of the cuprous solutions logically follows the principal operations, and it is natural to use this cement copper for the production of the sulphate of this metal.

But it must be remarked first that the direct attack of cement copper requires the use of heat, and involves a considerable loss of sulphuric acid given off in the form of sulphurous acid, according to the reaction $2\text{SO}_4\text{H}_2 + \text{Cu} = \text{SO}_4\text{Cu} + \text{SO}_2 + 2\text{H}_2\text{O}$.

Further, cement copper is always impure, and hardly ever contains more than 60 or 70 per cent of pure copper, and we can only obtain an equally impure sulphate of copper by direct attack, while trade requirements now limit the maximum proportion of impurities to only one and a half or two per cent.

Thus we are obliged first to proceed with the purification of the cement copper by melting, refining, and granulation, and to avoid the loss of the reagents we then oxidise the cement copper by roasting in muffle furnaces. This latter operation is costly, as it causes the disengagement of abundant fumes carrying with them considerable quantities of the metal; this loss is only partially obviated by the construction of dust chambers and condensation towers, in which the solid matter escaping from the furnaces is collected.

It is to remedy these imperfections that I have endeavoured to find a process for the commercial production of sulphate of copper, starting directly from the sulphurised ores, or from poor mattes, and without submitting the metal to any intermediate preparation.

Direct Method for the Sulphating of Mattes or Ores.

The ore or matte, suitably broken up, is subjected to an oxidising roasting in a muffle furnace, sufficiently prolonged to transform the whole of the sulphide of copper into oxide or sulphate.

This result is only attained after the complete dissociation of the sulphate of iron, and the partial decomposition of the sulphate of copper formed. In practice we may consider that there is no more copper left in the form of sulphide when four-fifths of the sulphate of copper are transformed into binocide.

When the operation is complete, we remove the ore from the sole of the muffle furnace to the floor of a cooling chamber, through which the sulphurous gases from the oxidation of the sulphur and the dissociation of the sulphates are passed after mixing with a suitable amount of air.

These gases move with the ore, which is gradually shovelled towards the other end of the cooling chamber, opposite to the roasting furnace.

On account of the lowering of the temperature, a series of chemical changes is produced between the ore and the sulphurous gases, similar to those observed in Sainte-Claire Deville's hot and cold tube.

Thus we bring into the presence of the calcined ore a mixture of sulphurous anhydride and air, which, by the well-known catalytic action of peroxide of iron and sulphate of copper, forms sulphuric anhydride, which at a lower temperature transforms first the oxide of copper, and secondly, the peroxide of iron into sulphates. It is necessary to observe that on account of its higher tension of dissociation at the temperatures through which the ore

* A Paper read at the Fifth International Chemical Congress at Berlin, 1903 (Section II.).

successively passes, ferric sulphate cannot be formed until after the sulphate of copper.

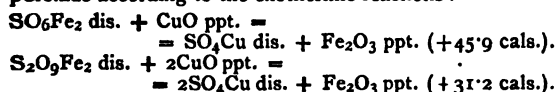
The transformation of the sulphurous anhydride into sulphuric anhydride begins to take place as soon as the temperature falls below 750° , and the speed of the reaction appears to be at its highest between 550° and 600° .

It is best not to let the temperature fall below 500° to prevent the formation of ferrous sulphate by the reaction $\text{Fe}_2\text{O}_3 + 2\text{SO}_2 + \text{O} = 2\text{SO}_4\text{Fe}$.

Finally, it is necessary to remark that above 500° , only basic ferric sulphates can be formed ($\text{S}_2\text{O}_5\text{Fe}_2, \text{SO}_6\text{Fe}_2$).

An idea that has been entertained by several inventors is that of limiting the reactions entirely to the sulphating of the copper, leaving the peroxide of iron intact, the surplus sulphurous gases being directed into an apparatus for the regeneration of sulphuric acid (lead chambers or an arrangement for oxidation by contact).

However, this regulation of the reactions is impossible, and I found that it is advantageous to produce, on the contrary, the largest possible quantity of basic ferric sulphate, which serves ultimately as the vehicle for carrying the sulphuric acid to other portions of the ore. The sulphated ore submitted, as has been said, to a methodical lixiviation, gives hot concentrated solutions, which are digested hot with ore that has been roasted sweet, and contains, consequently, the whole of the copper in the state of binoxide. The ferric sulphate sulphates the copper, while the iron is precipitated in the state of peroxide according to the exothermic reactions:—



Thus we obtain solutions of sulphate of copper relatively pure, and which are treated as we shall describe further on.

I may add that this method of sulphating is not indispensable, and that any method of roasting may be used if it is pushed to complete oxidation with subsequent sulphating by the wet method, as the purification we are about to describe completely realises the separation of the sulphates of iron and copper.

Purification of Solutions of Sulphate of Copper.

The impurities contained in raw solutions of sulphate of copper can be always reduced by means of separate crystallisations, to the presence of iron in the states of ferric and ferrous sulphate.

Then, to get the pure sulphate of copper, the ferric sulphate is reduced to the state of ferrous sulphate, and subsequently separated from the sulphate of copper by purely physical means, utilising the variations of the respective solubilities of the two salts at a high temperature.

From the researches of M. Etard on saturated solutions at high temperatures, it appears that the coefficient of solubility of pure sulphate of copper reaches a maximum at about a temperature of 100° , and then decreases very slowly. The solubility of ferrous sulphate is at its highest a little below 100° , and then diminishes rapidly, becoming nil at a temperature below 160° .

If we put the two salts into water simultaneously, we observe that their respective solubilities follow laws entirely different to those corresponding to solutions of the sulphates taken separately. The solubility of ferrous sulphate first increases with the temperature, more rapidly than that of sulphate of copper; then the variations change in direction, and above 100° the respective solubilities again take the course which characterises the isolated salts, so that at about 160° the whole of the sulphate of copper remains in solution, while the ferrous sulphate is completely precipitated.

From these observations I have devised the method for the separation of the two salts which I will now describe:—

The ore, sulphurised or otherwise, or the matte from which the sulphate of copper is to be extracted, is submitted to a preliminary treatment by which the metallic sulphides are transformed into sulphates, then to a

methodical lixiviation, so as to obtain, as I have described above, solutions of sulphates, as saturated and as hot as possible, containing sulphate of copper and a more or less high proportion of sulphate of protoxide of iron.

If the solution still contains a little ferric sulphate, a current of sulphurous acid is passed through it; this reduces the peroxide salt, and transforms it into ferrous sulphate.

The solution, maintained almost at a boiling temperature, is then filtered, and contains only sulphate of copper and sulphate of protoxide of iron. By means of a pump, it is forced into a tubular copper boiler, in which it is heated until the manometer shows a pressure of 10 kilograms.; that is to say, to a temperature of about 180° ; at this temperature the sulphate of protoxide of iron can no longer remain in solution, while the sulphate of copper is still very soluble.

We may remark here that it is advantageous to use concentrated solutions, but without allowing this concentration to reach the maximum saturation point for sulphate of copper, or a little sulphate of copper would be precipitated at the same time as the sulphate of protoxide of iron.

A concentration of 350 to 400 grms. of sulphate of copper per litre of solution is favourable to the separation.

It is necessary to have an active circulation in the tubes, to prevent the formation of deposits adhering to the sides of the tubes. Still, if such deposits are formed, they are easily removed when the boiler is not in use, by a simple washing with cold water.

The usual pressure is then used to drive the solution into a filter-press, of which the hollowed plates are heated by steam at 10 kilos. pressure, to delay the cooling of the solution as much as possible.

The cloudy liquid penetrates the cloths, where it leaves the suspended ferrous sulphate, while the solution of sulphate of copper runs in a clear stream into the crystallising vat. When the limited pores of the filter cloths are filled with the precipitate of ferrous sulphate, the operation is arrested, and the solution to be filtered passed through another filter-press.

The circulation of the steam being arrested, the plates are washed with pure water, which rapidly dissolves the sulphate of iron.

The solutions thus obtained are passed into a special reservoir for crystallisation.

The filter-press being now perfectly cleaned, it can be used at once for a fresh filtration, the operation being made continuous by the alternate use of two filter-presses.

We may also remark that the filter-press itself being cleaned by simple washing, there is no necessity to remove the plates except for the purpose of renewing the worn-out cloths.

The solutions of sulphate of copper are passed into wooden crystallising vessels lined with lead. Strips of lead are suspended in these vats, and the crystals of sulphate of copper attach themselves to them.

When the crystallisation is complete, which takes place in about five or six days, the mother-liquors are drawn off, and the crystals drained and dried in a centrifugal machine before packing.

The mother-liquors come again into circulation for the production of fresh solutions.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.
(Concluded from p. 45).

THE following articles and letters upon atmospheric dust and dust storms from other parts of the world are not only interesting, but they throw a great deal of light upon the subject of meteoric or atmospheric dust and dust phenomena.

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

nomena generally as experienced in Australia. Many more examples could have been given, especially if the meteorological publications had been laid under contribution; those given are some of those noted down in the ordinary course of reading.

Dust Atmosphere of China.—J. P. O'Reilly, Dublin, in a letter to *Nature*, January 17th, 1884, quotes from von Richtofen's work upon China, in reference to the dust atmosphere so characteristic of Central Asia, and more particularly of the loess district:—"Even during complete calms the atmosphere is often for many days yellow and opaque. The view is completely hemmed in, and the sun appears merely as a dull bluish disk."

More markedly is this character presented by these peculiar dust storms so well known to travellers visiting Tien-tsin and Pekin, and even more so to those who travel in the interior of the N.W. provinces of China. The wind then blows from Central Asia and everything becomes covered with a fine yellowish dust.

"In Schensi, where the air is rarely clear and transparent, the whole landscape has a yellow tint; streets, houses, trees, crops, and even the traveller one meets on the road, and the air itself, one and all, are yellow coloured" (see also Johnson's "Journey to Ilchi, the capital of Kotau," *Royal Geographical Society*, 1867, p. 5).

A writer in *Nature*, August 12th, 1886, p. 348, quoting from an article in the *American Meteorological Journal*, upon the dust storms of Pekin, says:—"These occur in the dry season, especially in the winter and early spring; they come on at irregular intervals, perhaps six or eight times in the season, and last about three days. The wind is W. or more often N.W. and blows fresh or high. The dust extends eastward from Pekin to the sea, and south-eastwards it regularly descends as far south as the Yellow River, and sometimes to Shanghai, 10° of latitude away."

The writer of the paper says this vast quantity of dust must come from the great deserts of Mongolia. He also refers to the variations in the barometer and thermometer accompanying the storms, and to the obscuration of the sun, which was set in a ring.

Dr. H. B. Guppy, in *Nature*, June 9th, 1881, says that in the spring of 1878 his attention was directed to the dust-winds which are of frequent occurrence in the valley of the Yang-tse, in the warm and dry season of the year. According to his observations at Hankow, they sometimes had the appearance of a dense mist, and at other times the air seemed to be penetrated by a fine haze, and in all cases a fine and impalpable dust was deposited, which was with difficulty excluded from the interior of the houses. Their duration lasted from a few hours to two days. He concluded that they are not local phenomena from the fact that one was experienced simultaneously from Hankow to Chinkiang, a distance of nearly 450 miles. The dust resembles the loess of the alluvial plains of the Yang-tse, and is generally made up of siliceous or calcareous particles from 1/1000 to 1/500 inch in size, and vegetable debris. From a study of the meteorological and electrical conditions of the atmosphere, he does not think they are due to sudden breezes.

Prof. S. P. Langley, of the Allegheny Observatory, Penn., in speaking of the red sunsets seen all over the world, says (*Nature*, January 31st, 1884) "we know of but two likely causes: one is the advent of an unusual amount of meteoric dust. While something over ten millions of meteorites are known to enter our atmosphere daily, which are dissipated in dust and vapour in the upper atmosphere, the total mass is small, compared with the bulk of the atmosphere itself, although absolutely large. It is difficult to state precisely what this amount is . . . approximately not greatly more than 100 tons, nor greatly less than 1000 tons a day."

"Taking the largest estimate as still below the truth, we must suppose an enormously greater accession than this to supply a quantity sufficient to produce the phenomenon in question; and it is hardly possible to imagine such a meteoric inflow unaccompanied by visual phenomena in

the form of "shooting stars," which would make its advent visible to all. Admitting then the possibility of meteoric influence, we must consider it to be nevertheless extremely improbable. There is another cause, which I understand has been suggested by Mr. Norman Lockyer—though I have not seen his article—that of volcanic dust."

Prof. Langley then speaks of the dust present in the apparently clear air of the upper parts of Mt. Etna, surrounded by snow field and deserts of black lava, yet the telescope showed that the air was filled with minute dust particles, which evidently had no relation to the local surroundings, but apparently formed a portion of an envelope common to the whole earth.

In 1881, Prof. Langley was on Mt. Whitney, Southern California, with an expedition from the Allegheny Observatory, where from a height of 15,000 feet they looked down upon a kind of level dust ocean, invisible from below, but whose depth was six to seven thousand feet. The colour of the light reflected from this dust was clearly red, and it stretched in every direction as far as the eye could reach, although there was no special wind or local cause for it. It was evidently like the dust seen in mid ocean from the Peak of Teneriffe; something present all the time and a permanent ingredient of the earth's atmosphere.

Mr. Clarence King, Director of the U.S. Geological Survey, thought that this upper dust was probably due to the "loess" of China having been borne across the Pacific and quarter of the way round the world. We were at the top of the continent, and the air which swept by us was unmingled with that of the lower regions of the earth's surface. Even at that great elevation the dust was perpetually present in the air, and I became confirmed in the opinion that there is a permanent dust shell enclosing the whole planet to a height certainly of about three miles, and probably to a height even greater. The meteorites which are consumed at an average height of 20 to 40 miles must add something to this."

E. Metzger, in a letter to *Nature*, Jan. 17, 1884, p. 261, draws attention to the presence of particles attracted by the magnet in the sand dunes near Scheveningen.

Some atmospheric dust collected at Klagenfurt, Carinthia, after a rain of mud, which had taken place on October 14, 1885, was found to consist of minute crystalline granules and flakes of quartz, opal, orthoclase, biotite, phlogopite, pyroxene, amphibole, mica, talc, kaolin, chlorite, rutile, anatase, zircon, tourmaline, ferruginous clay, spinel, magnetite, pyrites, magnetic pyrites, calcite, magnesite, dolomite, and apatite; metallic iron could not be found. Diatoms, &c., were present, together with a few carbonaceous or carbonised substances, such as the spores of fungi, filaments of algæ, &c., silicified membranes of parenchymal cellules, and pyritised and silicified spherules resembling pollen. Its reddish yellow colour, resembling the "Passat" dust, may be against its having come direct from the Sahara (Dr. M. Schuster, Imp. Acad. Vienna, January 14, 1886; and *Geol. Mag.*, 1886, p. 122).

In an address delivered to the Royal Meteorological Society, January 15, 1890, Dr. William Marcet, F.R.S., President, quotes from a paper by Dr. Cook in the *Trans. Roy. Meteorological Society*, who says that in India there are some days on which, however hard and violently the wind may blow, little or no dust accompanies it, while on others, every little puff of air or current of wind forms or carries off with it clouds of dust. If the wind which raises the dust is strong, nothing will be visible at the distance of a few yards, the sun at noon being obscured. The dust penetrates everywhere, and cannot be excluded from houses, boxes, and even watches, however carefully guarded. The individual particles of dust appear to be in such an electrical condition that they are ever ready to repel each other, and are consequently disturbed from their position and carried up into the air. Dr. Cook also describes dust columns and dust storms, and the electrical origin of both.

In a letter dated Tokio, April 23, Prof. J. Milne, F.R.S., states (*Nature*, June 29, 1892) that the commander,

Capt. R. Swain, of the S.S. *Yokohama Maru*, gave him a specimen of some dust which fell on the vessel on April 2, when about 95 miles west by south of Nagasaki, at about 6 p.m. The sun appeared quite yellow. The atmosphere was moist, and rendered everything upon the deck of the ship quite damp; the precipitated moisture was yellowish, and as it dried it left an extremely fine powder. For two days previously the wind had been blowing W.S.W., or from China. Nothing was felt in the eyes, and if the ship had not been covered with a yellow powder, the phenomenon would have been regarded as an ordinary but peculiarly coloured fog. . . . The probability is that the material came from the loess plains of China. At Nagasaki, which is 300 miles from the coast of China, a yellow sun was noticed on the morning of the 2nd, and during the day while the dust was being precipitated, the appearance of the atmosphere was compared to a London fog.

On April 1 there was a fall of dust at Nawa, in Okinawa-ken, and on the 2nd dust fell at Gifu. The P. and O. steamer *Verona*, which left Hongkong on April 1, experienced the same phenomenon as the *Yokohama Maru*, the vessel being covered with a fine dust, and there was so much haze that land was not seen until reaching Nagasaki. On April 3, a yellow sun was seen at Yokohama, but I am not aware that any dust was observed. Roughly speaking, it therefore seems that on April 2, at a distance of from 200 to 400 miles from the coast of China, there was a cloud of dust which may have been over 1000 miles and possibly 2000 miles in length. Dr. B. Koto, who examined the dust, tells me that the particles are chiefly felspar, but there is a little quartz and shreds of plants.

An article referring to a shower of dust in connection with snow in Indiana and Kentucky, appeared in the *Monthly Weather Review*, in 1895 (*Nature*, August 29, 1895, p. 419). The dust does not appear to have been the nuclei of the snowflakes, but was intermingled in the air with the snow, and fell during an interval between two snow storms. The examination of a large number of specimens showed that the dust was made up largely of silt, mixed with organic matter. A number of fresh-water algae were present, though they appear to have been dead and dried for some time. . . . Everything indicated that the material had come from the bottom of some dried up lake, pond, marsh, or river bed. The dust was almost identical with the so-called "loess" formation, which covers very extensive areas in Illinois, Indiana, Nebraska, and adjoining States, its depth in some places amounting to 100 feet or more. This is interesting, because there is a long standing controversy as to the origin of the "loess" of the north-west. Certain portions of the "loess" formation of Asia are known to be wind deposits, and there is very strong presumptive evidence, now borne out by the examination of the samples of dust, that much of the "loess" of the Western States is also a wind deposit. . . . This light soil is easily raised and carried off by strong winds of the western plains of America; instances have occurred in which six inches of surface soil have been blown away from freshly cultivated fields in the course of a single wind-storm.

J. M. Yates, writing from Davenham, Cheshire (*Nature*, April 1, 1897), says:—"On Tuesday morning, March 22, I noticed on the glass of our greenhouse and on many of the shrubs a sort of red dust. On making enquiries, I found the same thing existed about two miles due west. I collected some, and by the kindness of Messrs. Brunner, Mond, & Co., it was examined in their laboratory. The report says:—"The dust showed minute fragments of clayey matter, mixed with quartz; organic matter, such as pollen grains, was absent. The particles are about 0.0001 m.m. in diameter, many of them less. We are surrounded by grass; the soil is clayey loam, without oxide of iron or quartz."

A letter from Augusto Arcimis (*Nature*, April 21, 1898), in reference to the dust shower met with by the *Roslyn Castle*, off the west coast of Africa, describes the pheno-

menon as experienced at the City of Laguna, Teneriffe. "A light fog was observed from the early hours of the evening of February 15, with a light breeze from the east. During the night it rose to a moderate gale. At about 5 a.m. on the 16th a few drops of rain fell. The wind dropped to a gentle breeze again during the day, from the east. The fog became denser, and the sun pale and feeble like the moon. The drinking water became salty and coloured as by oxide of iron. The dust was grey and extremely fine, and was deposited on every object."

Some brown dust was collected on board the P. and O. S.S. *Sumatra*, during a thunderstorm in the Galita Channel, Mediterranean. Mr. G. T. Pryor (*Nature*, June 29, 1899) found the dust to be an argillaceous and calcareous sand, containing a little organic matter and a few angular grains of quartz.

Prof. Rücker, F.R.S. (now Sir Arthur Rücker), writing from Taormina, in Sicily (*Nature*, March 28, 1901), on March 12 to Prof. Judd, says:—"We have had a rather curious phenomenon here. The sirocco was blowing and the hills were wrapt in mist, but the fog assumed a yellow hue, and the sun, which at times could not be seen through it, was a bright blue. This was caused and accompanied by a copious fall of red dust. Some which I shook off my hat was quite dry, and on looking at it through a low power lens, all the granules appeared to be spherical, except a very few grains of what looked like quartz. . . . This dust also fell at Naples and Palermo in such quantity that the streets looked red, and the people were frightened." Prof. Judd states that under the microscope the dust is seen to be made up of particles of quartz, mica, &c., also frustules of fresh-water diatoms. Prof. Rücker (*Nature*, May 9) estimates the amount from his observation as about seven tons per acre.

Sir Ed. Fry, F.R.S., wrote to *Nature* from Failand, January 28, 1902, describing a fall of reddish or rust-coloured mud or dust, which covered greenhouses, plants, and clothing out to dry; it also fell at Lawrence Weston, about five miles to the N.E., Chewton Priory, some fifteen miles S.E., and Barry Island, some twenty miles W. by S., and on the other side of the Bristol Channel. The above fall was afterwards found to have spread over a large area, since it occurred in Cornwall.

On March 6, there appeared a letter in *Nature* from Mr. Clement Reid, stating that the above fall of red dust in South Wales may have been derived from the Red River dust flats, as he had noticed red dust clouds blown from the flats, and spreading across St. Ives Bay to St. Ives Head, a distance of over three miles. The wind was not a gale, but merely a strong dry east wind.

Gold and Platinum (?) in Meteoric Dusts.—For convenience, the results of the search for these metals are summarised here instead of being given under the headings of the various specimens examined. Minute quantities of gold were met with in two of the dusts examined, viz., from Gundagai and the University tank; that from the University beams also yielded a metal resembling platinum; some of the other dusts have yet to be tested. These metals were especially sought for when grinding and washing the dusts in an agate mortar to separate out the particles of metallic iron, as this is a much more delicate test for minute quantities of gold and platinum in such materials than any chemical test; they were obtained in the form of minute spangles.

The dust from the University beams, collected in 1882, from a portion of the roof some distance from the Chemical Laboratory, and completely cut off from it by several dividing walls and the ceilings, yielded a minute spangle of a white malleable metal, insoluble in nitric acid, even after evaporating the acid down to dryness; hence it appears to be one of the platinum metals. The particle was too minute to admit of applying other wet tests, hence it was not treated with aqua regia.

A dust from Muswellbrook (N.S.W.) yielded particles of a non-magnetic grey metal readily soluble in acid; this was probably zinc or zinc and lead from a galvanised iron

roof. Hartley and Ramage found lead in several meteorites, in volcanic and other dusts, as well as in chimney soots (*Proc. Roy. Soc.*, 1901).

The mud from the University tank, which may have been collecting for 30 years, as the tank had probably never been cleaned out since it was put up, yielded spangles of a yellow malleable metal, insoluble in nitric acid, even on evaporation, and therefore presumably gold; the metallic particles, although visible without a microscope, were very small and insufficient for the application of other tests. There were also present particles of a yellow metal resembling gold, but soluble in nitric acid; these may have been copper or brass (as copper is almost invariably present in meteorites it may have had a meteoric origin); the Mendie dust also contained a yellow metal soluble in nitric acid. The dust from Gundagai yielded yellow malleable metallic spangles insoluble in nitric acid, and therefore presumably gold.

In most cases some of the metallic spangles were visible without a lens; these were separated from the rest of the material left in the mortar by picking them up on the point of a needle and transferring them to a slide for examination under the microscope; under a one inch objective they still looked like gold; the action of the nitric acid was also watched in the same way; some of the soluble ones were seen to dissolve slowly, others quickly, with many minute gas bubbles.

The gold and platinum may or may not be of meteoric origin, but as both metals have been met with in meteorites (an account of the occurrence of gold in meteorites will be given in a subsequent paper), and platinum has apparently been previously found in meteorites (Davidson, *Am. Journ. Sci.*, 1898; Mingaye, "Report of the Dept. of Mines, Sydney," 1898, p. 21), it is not impossible that both the gold and the platinum metal may have had a cosmic source, although it is much more probable that the gold has been wind-borne from some auriferous area, for even the sandstone and shales about Sydney contain traces of gold (A. Liversidge, *Journ. Roy. Soc. N.S.W.*, 1894, pp. 185—188).

Conclusion.

I have quoted what may be considered by some as an unnecessarily large number of accounts of meteoric dusts, dust storms, rains of mud, dry fogs, &c., but I do so because some of the explanations given by different observers do not appear to quite account for the phenomena, and it appears to be desirable that sufficient evidence is needed for each to judge for himself. My own opinion is that the phenomena of dry fogs or haze, of dust storms, and mud rains are not due to extra-terrestrial causes; I think that the material or dust is mainly made up of debris, inorganic and organic, from the land, and occasionally, as everyone is aware, of volcanic dust; mingled with this undoubted telluric matter there appears to be nearly always a certain amount of extra-terrestrial or cosmic matter, i.e., the dust or debris of meteorites, although in most cases it is very difficult or even impossible to discriminate between the terrestrial and the cosmic dusts.

The presence of cobalt and nickel in the iron of a dust was formerly regarded as a proof of its meteoric origin, but it is now known that both of these metals occur in the metallic iron met with in some rocks, and notably in the telluric irons of Greenland; nickel has also been found in dust from volcanoes, and in the soot from coal smoke, by W. Noel Hartley, F.R.S., and Hugh Ramage (*Proc. Roy. Soc.*, March, 1901, p. 97). They also found other metals in soot, e.g., copper, gallium, thallium, silver, chromium, lead, &c. Both nickel and cobalt occur in some varieties of commercial iron and steel; cobalt is especially likely to be present in traces in Bessemer or other steel in which speigelleisen or other manganese alloy is used in the manufacture. A piece of a Sydney tram-rail, a horse-shoe picked up in the street, and nails from the same, all yielded traces of cobalt; nickel was not tested for, as the presence or absence of cobalt was regarded for the purposes of this inquiry as of more importance.

In spite of the presence of cobalt and nickel in some telluric irons, dusts, and soils, I still think that some, if not most, of the metallic iron (containing nickel and cobalt) found in dusts, such as have been described in this paper, is of meteoric or cosmic origin; the particles resemble those obtained from meteorites and do not look like pieces abraded from manufactured articles; further, they are not usually rusted to any great extent, whereas small particles of ordinary iron and steel (even if small amounts of cobalt and nickel are present) usually rust quickly; the difficulty is to prevent them passing wholly into the form of oxide; then too, the minute spheres of iron found in what are regarded as meteoric dusts and deposits are not found in flue dusts nor in volcanic dusts; as already pointed out, they have, however, been formed artificially by Prof. Schuster from meteorites.

The following shows, however, that a telluric form of spherulitic iron does occur:—In the *Transactions of the Royal Society of Canada* for 1890, Dr. G. C. Hoffmann describes an occurrence of metallic iron, containing nickel and cobalt, on St. Joseph Island, Lake Huron, Ontario. The iron occurs as minute spherules in a thin coating of limonite on the fissure faces of surface specimens of quartzite, the spherules amounting to 60 per cent of the coating by weight. The largest spherules are about 0.3 m.m. in diameter. Sp. gr. 6.86. The part of the spherules soluble in hydrochloric acid contained:—

Iron	97.79
Magnesia	0.57
Nickel	0.11
Cobalt	0.23
Copper	0.10
Sulphur	0.13
Phosphorus	1.07

100.00

The portion insoluble in hydrochloric acid (non-metallic), 9.76 per cent, was made up of spherical and ovoid grains, and consisted mainly of silica. The spherules were made up of a siliceous nucleus, coated with a humus like substance, which in turn was covered with the metallic layer; the author suggests that this metallic layer was probably due to the reduction of an iron salt by organic matter.

The presence of a nucleus of silica or other non-metallic matter in the spherules, regarded as of cosmic origin, has not been recorded; further, the meteoric spherules show traces of fusion, hence I think the Canadian spherules are quite distinct.

Finally, although there appears to be no doubt whatever that there is a constant gentle rain of meteoric dust falling upon the earth's surface, and at times it is probably greater than at others, especially after the periodic meteor displays, the evidence certainly does not show that the dust storms, dust, haze, red rain, mud showers, &c., are due to any unusual descent of meteoric matter; hence it is a misnomer to call the deposits from such "meteoric dust."

Experiments on Plaster-of-Paris; the Setting of Plaster.—Ch. Cloëz.—When anhydrous plaster is thrown into a certain quantity of water, the temperature rises rapidly to 14—22° above the original temperature, then in about ten minutes it drops from 4° to 6°, and remains stationary for some time, and finally rises again, reaching a point higher than the one it first went to. This series of phenomena is absolutely independent of the amount of water used for mixing. Experiments were made, and the results are shown in curves, to determine the best proportion of water and plaster necessary to obtain sufficient hardness when the plaster was set. The setting of the plaster is proved to be due to the succession of the following three phenomena:—1, Hydration; 2, solution; 3, solidification of a supersaturated solution.—*Bull. Soc. Chim.*, Series 3, xxix., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 26, June 29, 1903.

Influence of Non-saturated Radicles on the Rotatory Power of Active Molecules. α -Allyl- or Propyl- δ -methyl- β -cyclopentanonecarbonic Ethers.—A. Haller and M. Desfontaines.—Unsuitable for abstraction.

Oxidation of Manganese Salts by Alkaline Persulphates in Acid Liquor.—H. Baubigny.—In neutral solution the oxidation of manganese salts by alkaline persulphates is stopped by the immediate formation of a brown colour, which is accentuated by the action of heat. In acid medium, on the contrary, the action takes place less violently, especially if slowly heated, and at first a pale rose colour appears like the ordinary colouration of permanganic acid. This disappears to give place to a brownish-black precipitate of oxide, the liquid above once more becoming slightly rose coloured. The author's researches were specially directed towards the action of KMnO_4 on an acid solution of MnSO_4 .

New Plumbic Derivatives. Preparation; Thermochemical Investigation.—Albert Colson.—The decomposition of plumbic tetracetate by the fixed acids is comparable to the decomposition of ordinary salts, and allows of the preparation of plumbic derivatives, which do not have the ordinary action on minium nor the action with chlorine which ordinary lead salts possess. To prepare such salts it is necessary to operate in a vacuum and to keep the temperature low, otherwise reduction takes place and normal salts appear.

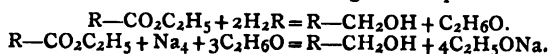
Organic Base containing Phosphorus. Its Constitution and Certain of its Salts.—P. Lemoult.—The reaction of PCl_5 on boiling aniline is often very violent, but can be employed to obtain a hitherto unknown derivative of pentabasic phosphoric acid, $\text{P}(\text{OH})_5$. The reaction, however, does not take place according to theory, giving as it would $\text{P} \equiv (\text{NHC}_6\text{H}_5)_5$, but stops with the formation of a tetranilide compound, chlorophosphotetranilide, $\text{PCl}(\text{NHC}_6\text{H}_5)_4$, a substance already obtained by Gilpin. The reason of the apparent stopping of the reaction is due to the fact that this body is not an acid chloride, but the chlorohydrate of a new base, which the author now isolates, and obtains salts with HCl , H_2SO_4 , HNO_3 , and chloroplatinate. The base is trianilidophenylphosphimide, $(\text{C}_6\text{H}_5\text{NH}) \equiv \text{P} = \text{NC}_6\text{H}_5$.

Volumetric Estimation of Nitric Acid.—M. Débourdeaux.—The author devises a method of estimation of nitric acid which does away with a number of the practical difficulties connected with the ordinary volumetric analysis of nitrates, and presents the following advantages:—(1) A liquid scarcely alterable by contact with air is used; (2) a sulphuric medium remains which renders titrations very easy; (3) the use of carbonic dioxide is avoided; (4) the estimation is very rapid; (5) the results obtained have an accuracy within $1/200$ th of the whole. The method is based on the action of nitric acid on oxalic acid. The proportion of oxalic acid destroyed is determined by an estimation with permanganate of potash.

Silicon Amide and Imide.—Em. Vigouroux and M. Hugot.—Silicon amide results from the action of ammonia on silicon chloride at a temperature lower than 0° . When the temperature rises above 0° the amide slowly loses ammonia gas, and a residue is left which is the imide, $\text{Si}(\text{NH})_2$. At 120° the decomposition is complete. Both bodies are thus prepared in a state of purity, as can be shown by analysis.

Compounds of Hydroferrocyanic Acid with Organic Bodies.—MM. Chretien and Guinchant.—Hydroferrocyanic acid forms with ether a compound containing 1 mol. of acid and 2 mols. of ether. This compound is only formed or destroyed under the influence of catalytic agents, such as water vapour. It can absorb up to 0.71 mol. of ether at 0° , giving a solid solution whose concentration varies with the temperature and with the tension of the vapour in the surrounding medium.

Preparation of Primary Alcohols by means of the Corresponding Acids.—L. Bouveault and G. Blanc.—The primary alcohols can be prepared by reducing an aldehyde, $\text{R}-\text{CHO}$, by means of sodium amalgam. The aldehyde is first produced by calcination with calcium formate from the calcium salt of the acid, $\text{R}-\text{CO}_2\text{H}$, or by another method a chloride or anhydride of the acid is reduced by sodium amalgam or a zinc copper couple. Both these methods give a poor yield of alcohol. The authors improve on these methods, and find that the methylic or ethylic ethers of the fatty acids are reduced by sodium in presence of absolute alcohol according to the equations:—



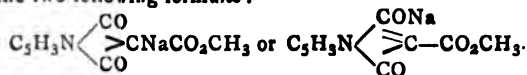
MISCELLANEOUS.

British Association (Section B), 1903.—In his opening Address to the Section, the President, Prof. W. N. Hartley, F.R.S., proposes to give a brief account of twenty-five years' work in Spectroscopy applied to the investigation of the composition and constitution of terrestrial substances, both organic and inorganic, and to review the present position of spectroscopy chiefly in relation to chemical theories, indicating where it may be usefully and profitably extended. The following papers will be read:—

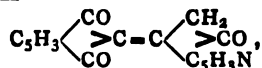
- "Dynamic Isomerism," by T. M. Lowry, D.Sc.
- "Hydroaromatic Compounds," by Dr. A. W. Crossley.
- "The Cause of the Lustre produced on Mercerising Cotton," by J. Hübner and W. J. Pope, F.R.S.
- "Mutirotaion and the Glucoside Constitution of Glucose," by Dr. E. F. Armstrong.
- "A Contribution to the Constitution of the Disaccharides," by T. Purdie, F.R.S., and J. C. Irvine, D.Sc.
- "Some Derivatives of Fluorene," by Miss Ida Smedley.
- "Fluorescence as Related to the Constitution of Organic Substances," by J. T. Hewitt, D.Sc.
- "The Cholesterol Group," by Dr. R. H. Pickard.
- "On Essential Oils," by Dr. O. Silberrad.
- "Freezing-point Curves of Binary Compounds," by J. C. Philip, Ph.D.
- "Action of Diastase on the Starch Granules of Raw and Malted Barley," by A. R. Ling.
- "Action of Malt Diastase on Potato Starch Paste" (Part I.), by B. F. Davies, B.Sc., and A. R. Ling.
- "Action of Malt Diastase on Potato Starch Paste" (Part II.), by A. R. Ling.
- "Some Properties of Sodium Hydride," by A. Holt.
- "On a Method of Separating Cobalt and Nickel and the Volumetric Determination of Cobalt," by R. L. Taylor.
- "The Influence of Small Quantities of Water in bringing about Chemical Reaction between Salts," by E. P. Perman, D.Sc.
- "Sur le Spectre du Silicium," and "Sur les Procédés de Photographie Spectrales applicables à la pratique des Laboratoires de Chimie," by M. le Comte Arnaud de Gramont.

Dr. W. A. Bone will open a discussion on the general question of Combustion by a paper on the Combustion of Methane and Ethane.

Synthesis of Pyridinic Derivatives.—K. Bittner.—Quinolein dicarbonate of methyl, $C_5H_3N(CO_2CH_3)_2$, dissolved in acetate of methyl, and treated with sodium when heated to 80° , gives a salt of sodium which is precipitated by ether from its alcoholic solution. This salt crystallises in yellow needles, which become resinified immediately on contact with the air. It answers to one of the two following formulæ:—



On the addition of hydrochloric acid we obtain yellow needles soluble in water; they consist of *pyridanedione-carbonate of methyl*, $C_{10}H_7NO_4$. The barium salt occurs in yellow needles. The *monoxime*, $C_{10}H_7O_4N_2$, is also in yellow needles, soluble in boiling water. *Anhydro-bis-pyridanedione*,—



is obtained by the action of heat at 100° , on the previous sodium salt, in acetic solution. It forms violet flakes insoluble in the usual solvents, but is soluble in concentrated acids giving a green solution, and in concentrated alkalis giving a blue solution.—*Berichte*, vol. xxxv., p. 1411.

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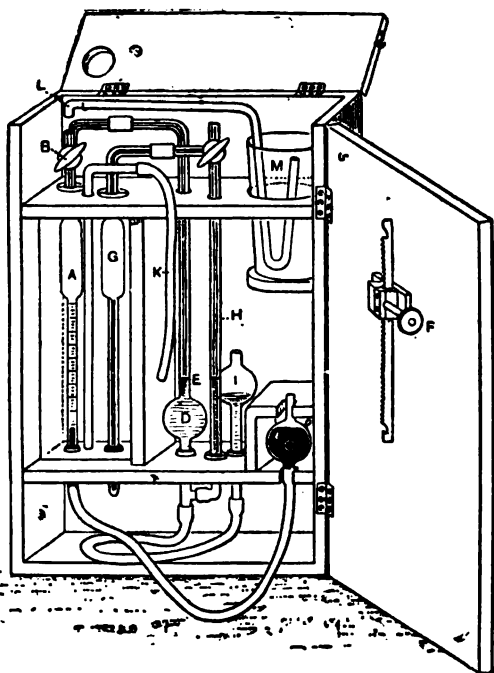
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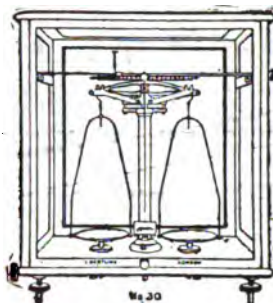
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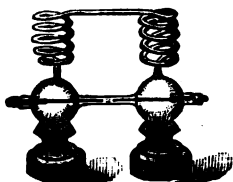
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2280.

ON POLONIUM AND THE INDUCING CHARACTER OF RADIUM.

By F. GIESEL.

It has been found by Marckwald (*Berichte*, 1902, xxxv., 2285, 4239) that metallic bismuth, which is immersed for some time in a hydrochloric acid solution of Curie's bismuth polonium, acquires to a remarkable extent the property of emitting α -rays. Marckwald considers that the precipitate formed on the bismuth consists, at any rate in part, of metallic polonium, and regards the electrolytic separation as the proof of the existence of an (electro-negative) element differing from bismuth and allied to tellurium.

I (*Berichte*, 1902, xxxv., 3608) was successful in confirming Marckwald's observation with my purified polonium preparations, only no trace of a precipitate or a colouration was to be seen on the bismuth. As the non-appearance of a precipitate seemed to argue against Marckwald's theory, and in any case the prospect of obtaining sufficient quantity of the element in question was very remote, I tried to approach the question of the nature of polonium in a different manner.

In attacking this problem, I was guided by the opinion which I had previously expressed, that polonium may be bismuth acted upon inductively by radium, a view which was forced upon me by experience in direct experiments repeatedly performed when preparing preparations of polonium (*Berichte*, 1902, xxxv., 3610). As in my earlier experiments, less attention had been paid to α -radiation, and I had recently found (*Berichte*, 1903, xxxvi., 729) that this was developed both in metallic bismuth and also in platinum and palladium by the action of a solution of bismuth polonium chloride, it was important to investigate how a radium solution would behave. It may be safely asserted that the clean surface of the metals guaranteed the possibility of perfectly removing every trace of the *soluble* primarily active reagent, which cannot be vouched for in the case of precipitates even with the most careful washing. This appears all the more important when it is remembered that even one-half a millionth part of radium salt, present as an impurity, is sufficient to cause appreciable phosphorescence of the barium platinum cyanide screen.

In fact, it is now easily possible to impart to bismuth or the platinum metals, by *momentary* contact with radium, properties which exactly resemble those produced by polonium.

If a freshly cut piece of bismuth is placed in a solution of 0.01 grm. radium bromide in 1 c.c. water, after remaining there for one to two days, the bismuth shows strong α -radiation and no β -radiation.

NOTE.—The non-appearance of β -radiation, after keeping for two weeks, may perhaps be employed as a control experiment for demonstrating the absence of radium. For testing for α -rays the zinc sulphide screen was used, and for β -rays the barium platinum cyanide screen. All α -radiation produces on the zinc sulphide screen the scintillation described by Crookes, and observed by Elster and Geitel, while the β -radiation appears to produce only uniform illumination. The effect of a current of air on the scintillation can only be observed in the emanation of my emanation substance (*Berichte*, 1903, xxxvi., 342).

The greatest possible care was taken to remove every trace of radium salt from the bismuth.

Platinum-wire and palladium-foil, before being introduced into the radium solution, were rubbed with emery and sea-sand, washed with hydrochloric acid and distilled water, and ignited. After treating with the radium solution, like the bismuth, they were carefully washed with

hydrochloric acid and distilled water to free them from the radium salt.

Bismuth is decidedly superior to the platinum metals in acquired activity, and seems to be best suited for accumulating the positive electrons of radium. It is noteworthy that the part of the platinum wire which was beyond the end immersed in the radium solution in the test-tube, and thus was only in contact with the air, also showed decided activity (α -radiation). The line of separation of solution and air was marked on the wire by a short zone of greatly diminished activity.

The α -radiation thus artificially communicated by the radium to the bismuth, palladium, and platinum shows no decrease, as far as has been observed. As it has hitherto always been found that the activity caused by induction diminishes with the time, comparatively speaking quickly, it is of great importance to investigate the limitations of this law by the manner and kind of induction, for which a longer time of observation is necessary.

The small quantities of bismuth and palladium passing into the hydrochloric acid solution in the above experiments were precipitated with sulphuretted hydrogen. The precipitates (especially the palladium sulphide), in spite of repeated washing, emit β -rays strongly. From what has already been said it could not be deduced whether this radiation is due to the adherence of radium; it can only be shown how it behaves with regard to the constancy of the activity.

I was able also to confirm the observation of the Curies, concerning the development of heat by radium, which can be proved in a very simple way.

If a thermometer is lowered into a glass flask containing 0.7 grm. radium bromide, in a short time it rises 5° above the temperature of the surroundings, and remains at this temperature as long as it is kept in the flask. When held over a capsule closed with a sheet of mica and containing 0.3 grm. radium bromide, the thermometer showed an increase of temperature of almost 2°, if it was protected from currents of air.—*Berichte d. Deutsch. Chem. Gesell.*, 1903, xxxvi., 2368.

THE ACTION OF MERCUROUS NITRATE AND OF THE NEUTRAL MERCUROSO-MERCURIC REAGENT ON ANTIPYRINE.

By A. MOULIN.

In a previous paper, in February, 1901, we described the action of the neutral mercurioso-mercuric reagent, as prepared by M. Causse (*Bull. Soc. Chim.*, vol. xliii., p. 493), on asparagin, dulcin, and saccharin.

This reagent reacts easily on these compounds, giving substitution compounds by the fixation of mercury on the amidised group.

With dulcin, if we work with hot solutions, the reaction is more complex; there is a decomposition of the molecule, and the formation of cyanate of mercury, and of a violet colouring matter described by Kingel. The reaction, which is easy to obtain, was described in our inaugural thesis (Lyon, January, 1902). The action of this reagent on antipyrine is much more complex, and gives rise to the formation of interesting nitro and nitroso-compounds.

I.—Action of Mercurioso-nitrate on Antipyrine.

If we dissolve antipyrine in a saturated solution of nitrate of potassium, and add a solution of mercurous nitrate dissolved in water saturated with nitrate of potassium, an abundant precipitate is formed immediately, having a greyish appearance, and consisting of beautiful colourless needles. The grey appearance is due to the presence of numerous globules of mercury.

The precipitate thus obtained is taken up with boiling alcohol at 60°. On cooling, small white crystals are deposited, slightly soluble in water; soluble in alcohol, especially when heated; soluble in nitric acid, even when

very dilute. Soda and ammonia also dissolve them. They are soluble in sulphuric acid, giving a red solution; they answer to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg$.

Analysis gives the following figures:—

		Found.	Theory.
C		24.58 and 24.96	25.78
N		9.98 " 10.13	10.93
Hg		38.68 " 38.47	39.06

II.—Action of the Neutral Mercurous-mercuric Reagent on Antipyrine.

This reagent is obtained easily in the following manner. 50 c.c. of mercury and 1 litre of a mixture of equal parts of water and concentrated nitric acid are placed in a flask. After the complete solution of the mercury, a current of air is passed through to remove the nitrous fumes; the flask is then left to stand in a dark place until the contents are completely decolourised. Measure off 100 c.c. of this reagent, and add 400 c.c. of a saturated solution of nitrate of potassium; heat on the water-bath, and add some yellow oxide of mercury until saturated; allow to cool and filter.

If we add this reagent very gradually to a solution of antipyrine, we soon notice the formation of a white gelatinous precipitate, which is at first dissolved on stirring and afterwards permeates the entire liquid, which becomes green. The flask in which the reaction has been effected is then placed on the boiling water-bath. The precipitate becomes crystalline, and takes a reddish tinge, with a tendency towards yellow. Allow to cool, and collect the precipitate, which is washed and dried over sulphuric acid. The product thus obtained has not a constant composition, it is formed of a mixture, and it is necessary to purify it.

For this purpose, the crystalline powder obtained is treated with concentrated nitric acid until this acid no longer takes a brown colour. A bright red powder remains, slightly soluble in water, which it colours a reddish yellow; it is slightly soluble in nitric acid; sulphuric acid appears to dissolve, but in reality decomposes it. Ammonia transforms it into a brownish yellow compound. The compound thus obtained answers to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg_2$.

Analysis gave the following results:—

		Found.	Theory.
C		19.96 and 20.01	19.41
N		8.31 " 8.40	8.23
Hg		59.18 " 58.10	58.82

The nitric acid used for the washing of this body is coloured strongly brown. It is diluted with a large quantity of water, when a precipitate is formed immediately. It is left for twenty-four hours, and the precipitate is collected on a filter, washed with distilled water, and dried over sulphuric acid.

It occurs in the form of a crystalline powder, of a chamomile yellow colour; it is soluble in nitric acid, and partially so in sulphuric acid; it is very slightly soluble in water, and answers to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg$.

Analysis gave the following results:—

		Found.	Theory.
C		26.30 and 26.91	27.50
N		10.73 " 11.31	11.66
Hg		40.01 " 41.06	41.66

These two compounds explode when heated to 205–210°, they decompose with violence, leaving a voluminous carbonaceous residue, and give off a gaseous product having a strong odour of garlic; at the same time they deposit a yellowish powder which we have not yet examined.

The mother liquors resulting from the preceding operations are evaporated on the water-bath, then on the sand-bath, but the temperature must not rise above 140°; the residue, after washing with distilled water, appears as a reddish-yellow powder with a crystalline texture, and is

no other than the compound $C_{11}H_{12}N_2O(NO_3)_2Hg$, previously described and obtained by quite a different method. The colouration in this case is due to traces of nitroso compounds, which we have not been able to remove entirely.

Conclusions.

Mercurous nitrate reacts easily on antipyrine in solution, giving a nitro-mercurate of antipyrine, answering to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg$.

The action of the neutral mercurous-mercuric reagent is much more complex. There is first the formation of the preceding compound, and at the same time the formation of nitroso-mercurous antipyrine and nitroso-mercuric antipyrine, which are easily distinguished by their colour and their solubility in nitric acid, decomposing with explosive force at about 205°, and answering to the formulae $C_{11}H_{12}N_2O(NO_3)_2Hg_2$ and $C_{11}H_{12}N_2O(NO_3)_2Hg$.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 5.

NOTE ON THE

ELECTRO-METALLURGY OF ALUMINIUM.*

By GUSTAVE GIN.

Choice of the Electrolyte.

IN solution, in a fused salt, the compounds of aluminium can be electrolysed with the mono- or bivalent metalloids.

The electrolysis of the double salts may be compared with that of the binary compounds in this sense, that there is a primary decomposition of the complex molecule, then dissociation of the binary constituent, which is the least exothermic under the conditions of the experiment.

The electrolytic bath, comprising the electrolyte (properly so-called) and its solvent, ought to satisfy the following physical conditions:—The fusing-point must be high; when fused, the electrolyte must be of suitable fluidity, and of a density lower than that of melted aluminium; it should have very little vapour-tension and an electric resistance as low as possible.

From the chemical point of view, the compound to be electrolysed should be chosen from among the least exothermic. This condition is not so rigid as the preceding ones, but it corresponds to the minimum expenditure of energy, and it is as well to appreciate its importance.

Now, for any particular electrolyte, as the weight of the aluminium set free depends only on the amount of electricity used, it results that the energy used is exactly proportional to the tension of the bath. Now this tension is divided into two parts, of which one is a function of the resistance of the bath, the distance apart of the electrodes, and the strength of the current. The other portion—that is to say, the tension of polarisation—corresponds to the passage of the ions to the molecular state, and it depends on the heat of formation of the electrolyte, which comprises the heat of the ionisation of the constituents.

Our knowledge of the properties of fused salts is much less complete than that of aqueous solutions, and is quite insufficient to enable us to solve all the difficulties of calculating the tension of polarisation.

However, we may presume that, in igneous solutions of the haloid salts of aluminium, dissociation is almost complete, and this presumption appears to be verified in the electrolysis of fluoride of aluminium, concerning which Minet has collected observations of great exactitude.

If the ionisation is complete, the heat corresponding to the tension of polarisation is equal to the sum of the heats of ionisation of the anion and of the cation, and we shall have—

$$Q = J_F + J_{A_1} = 50750 + 40100 = 90850 \text{ c. gr. d.,}$$

* A Paper read at the Fifth International Chemical Congress at Berlin, 1903 (Section X.).

† These conditions were formulated by Minet at a time when electro-chemical research was very much more difficult than it is to-day.

which corresponds to a tension of—

$$E = \frac{90850}{23067} = 3.93 \text{ volts.}$$

As a matter of fact, Minet found only 2.5 volts experimentally, but the disagreement is only apparent, and is caused by not taking into account the secondary reactions produced by the liberated fluorine in the above calculation.

In a communication to the Congrès de Metallurgie de 1900, M. Heroult admitted that in the electrolysis of cryolite no fluorine is given off, and that an acid fluoride of sodium is formed, soluble in water; that is to say, that in the decomposition of Al_2F_6 , the 6NaF would correspond to the formation of 6 molecules of the compound NaF_2 . Now, as the mono-atomic elements are only able to form one single series of compounds among themselves, the body NaF_2 cannot exist, and it is probable that the soluble body observed was simply fluoride of sodium forming the residue of the decomposed cryolite.

It is quite true that fluorine is not given off in the free state, but in the form of a tetrafluoride of carbon mixed with a more highly carburetted fluoride.

Further, this reaction has the greatest analogy with that which accompanies the electrolysis of alumina in solution, which gives carbonic acid mixed with carbonic oxide at the anode.

Now, if we take into consideration the reaction of the fluorine on the anode, the preceding formula must be written—

$$Q = J_F + J_{Al} \frac{1}{2} - \text{the heat of formation, } \text{C}_4\text{F},$$

or—

$$Q = 50750 + 40100 - 33400 = 57450,$$

from which we get—

$$E = \frac{57450}{23067} = 2.49 \text{ volts,}$$

a figure which coincides with that found by Minet.

Electrolysis of Al_2O_3 .

Let us pass now to the electrolyte of Heroult and Hall, in which it is oxide of aluminium that is decomposed. We shall have—

$$Q = J_{O\frac{1}{2}} + J_{Al} \frac{1}{2} - \text{the heat of formation, } \text{C}_4\text{O},$$

$$= 34950 + 40100 - 24400 = 50650 \text{ c. gr. d.,}$$

from whence we get—

$$E = \frac{50650}{23067} = 2.19 \text{ volts.}$$

In applying the method of Max Le Blanc for the measurement of the tension of polarisation of a fused bath containing $\text{Al}_2\text{O}_3 + (\text{Al}_2\text{F}_6.6\text{NaF})$, I found 2.3 volts as the mean of four observations.

Electrolysis of Al_2S_3 .

For sulphide of aluminium we have—

$$Q = J_S \frac{1}{2} + J_{Al} \frac{1}{2} - \text{the heat of formation, } \text{C}_4\text{S}_4.$$

But the heat of formation furnished by the tables corresponds to S in the solid state, while the compound CS_2 is formed from S in the gaseous state. We get a closer figure to the heat of formation by adding to the number in the table the heat of volatilisation calculated by de Forcrand's formula; that is, 21600 c. gr. d. for $T = 720^\circ \text{C}$.

Under these conditions, the heat of formation of C_4S , instead of being negative, becomes positive, and passes from -6450 to +4350.

Therefore we get—

$$Q = -6300 + 40100 - 4350 = 29350 \text{ c. gr. d.,}$$

from whence we have—

$$E = \frac{29350}{23067} = 1.27 \text{ volts.}$$

From the above figures we calculate that, for the preparation of 1 kilogram of aluminium by means of the electrolytes dealt with, the energy consumed will be given

approximately by one of the following formulæ, in which K_F , K_O , and K_S are quantities varying between 16 and 19 kilowatts:—

$$\begin{array}{lll} \text{For } \text{Al}_2\text{F}_6 \dots \dots T = (K_F + 8.5) \text{ K.W.H.} \\ \text{Al}_2\text{O}_3 \dots \dots T = (K_O + 7.5) \text{ " } \\ \text{Al}_2\text{S}_3 \dots \dots T = (K_S + 4.4) \text{ " } \end{array}$$

The maximum difference between the various electrolytes is thus probably about five kilowatt-hours. At the present price of electric energy furnished by large water-falls, this difference represents only a few centimes per kilogram of aluminium.

Thus we find that the cost of the aluminium depends much less on the more or less easy decomposition of the electrolyte than on the cost of that electrolyte. The economic problem is therefore of a chemical rather than an electro-chemical order.

I have one more interesting remark to make before finishing:—In electrolysing a mixture of artificial cryolite and sulphide of aluminium, and stopping the operation before its completion, I observed the presence of a sub-sulphide of aluminium in the electrolyte; it was distinctly crystalline, and of a bright cinnabar-red colour. I am following up the examination of this compound, the existence of which could be foreseen from the work of M. Sabatier.

CHLORINE SMELTING, WITH ELECTROLYSIS.*

By JAMES SWINBURNE.

Argument.

CHLORINE smelting, a new process covering wide domain in metallurgy. Present processes, furnace reductions. Costly and give impure metals. Can only treat certain ores. Chlorine process treats pure sulphides, and gives still better results on mixed or refractory sulphides. Process is in three stages; writing Zn for Zinc, and M and N for other metals:—I. $\text{ZnS} + \text{MS} + \text{NS} + 3\text{Cl}_2 = \text{ZnCl}_2 + \text{MCl}_2 + \text{NCl}_2 + 3\text{S}$. II. $\text{ZnCl}_2 + \text{MCl}_2 + \text{NCl}_2 + 2\text{Zn} = 3\text{ZnCl}_2 + \text{M} + \text{N}$. III. 3ZnCl_2 electrolysed = $3\text{Zn} + 3\text{Cl}_2$. More detailed description. Working cost of process. Capital cost. Antimony. Arsenic. Bismuth. Cobalt. Copper. Gold. Iron. Manganese. Nickel. Silver. Tin. Zinc. Rule for capital.

Present Processes.

It will seem rather late in the history of metallurgy to bring forward a scheme which aims at nothing less than a complete revolution of the major part of the art of metallurgy, but this is a new Society, and it is but fitting that a new process be brought before it for discussion and probably criticism, but I hope for and expect help in the way of suggestions and information from many of the members who are especially qualified to give it.

At present we may take it the normal process for obtaining a metal is to convert it into oxide and reduce the oxide by carbon. Iron is a good example. It occurs as oxide, and is reduced by carbon or its monoxide. The result of this process is a metal which is very cheap, but very impure. The economical value of pure iron is unknown. It may be very high. More will be said about that presently.

Zinc is obtained purely by reduction, though work has been done on its extraction by electrolysis, especially from aqueous solutions. The bulk of the zinc of the world is obtained by a very crude method of reduction by carbon. Copper involves a furnace reduction process which may be partly classed as carbon reduction, and partly as a direct action analogous to the alternating reduction of lead sulphide. Tin is reduced by carbon. Electrolysis has come to the front, however, in the reduction of sodium and aluminium.

The great drawback to the carbon reduction processes is

* A Paper read before the Faraday Society, June 30, 1903.

that the metals so obtained are always impure, the refining often being exceedingly expensive; there is a great deal of waste, and many mixed, or so-called refractory ores, cannot be treated at all.

Electrolysis provides an admirable means of getting many of the metals down, but the difficulty is generally in getting the metal from the ore to a suitable condition for electrolysis. Thus copper is very easily deposited from, say, copper sulphate solution, but it is by no means easy to prepare a copper sulphate solution economically from a copper ore.

There is also difficulty as to the anodes. Carbon is corroded, and lead or antimonial lead need a still higher electromotive force. Aqueous solutions of lead salts cannot be made economically from lead ores, and their electrolysis gives rise to lead sponge, which cannot be dealt with. Zinc gives similar troubles.

What is wanted to displace furnace reduction of oxides and sulphides is to convert the ores into salts of the metals that can be easily and cheaply electrolysed, and to do this simply, efficiently, and economically.

The Chlorine Process.

The process I have the honour to bring before the Society is simplicity itself. The sulphide ore is treated with chlorine so as to displace the sulphur and absorb all the chlorine. The chloride is then electrolysed to get the metal and recover the chlorine. This is the process in its naked simplicity. When all the details necessary, even in connection with complex ores, are considered, in comparison with existing methods, the process is exceedingly simple.

As a good example, suppose pure galena is to be smelted. The galena is treated with hot chlorine, so as to form lead chloride and sulphur. The sulphur is condensed as brimstone, and the lead chloride is electrolysed in the fused state, producing lead and chlorine. If there is silver or gold present, the fused chloride of lead is treated with metallic lead. This replaces any gold or silver there may be, and the precious metals alloy with the remaining lead, so that ultimately a bullion is produced as rich as may be desired, the only limit being its melting-point, which must not be too high. The cost of de-silvering by the ordinary processes is thus saved. This process thus recovers all the lead, all the silver and gold, and nearly all the sulphur. If the electrolyte vats were so tight that no air got in, all the sulphur would be saved, but in practice a little sulphur is always burned into SO_2 .

Pure or nearly pure lead sulphide is easy to smelt in the ordinary way; but this smelting does not separate the silver, and is thus incomplete. In time, therefore, the chlorine process is likely to replace the present methods, even for pure ores.

Take another example, pure zinc sulphide; the process is exactly analogous to that for pure galena. But in practice zinc blende contains gangue and generally iron, and these must be separated.

One of the great advantages of the chlorine process is that it is applicable to mixed ores, which are often absolutely refractory and useless otherwise. This process makes concentration quite unnecessary, unless merely for eliminating gangue, as the presence of several metals gives rise to no difficulty. In no case has one metal to be lost in order to extract another; and in no case is a metal brought out impure or needing refining.

Take, for example, a mixture of sulphides of lead, zinc, and iron, with some silver. An immense amount of work has been done on this class of ore, and great progress has been made in concentrating, so that one part will leave enough zinc to be worked, and little enough lead not to interfere with the metallurgy, and the other part will leave enough lead and little enough zinc. Each portion is smelted for one metal only, the other being worse than wasted, as it is a nuisance. An intermediate ore, often a large proportion, is thrown away.

The new process takes the ore just as it comes from the

mine, without any previous treatment; or, better still, it takes the slimes, such as the Broken Hill slimes, which are at present accumulating as a monumental memorial to the barbarity of presenting smelting processes. The slimes contain zinc, lead, iron, silver, and gangue. Hot treatment with chlorine converts the whole of the metals into chlorides, producing a broth of mixed fused chlorides and gangue. The silver is extracted by substitution of lead, the lead is extracted by substitution of zinc, and the iron is thrown out as ferric oxide, not as metal, zinc oxide being used as substitute, and the gangue is got out by filtration. We have then nothing left but zinc chloride, and this is electrolysed to yield zinc and chlorine.

The process thus consists of three essential elements:—

Treating the ores with chlorine.

Chemical treatment of the mixed chlorides, by substitution, so that all the chlorine is combined with zinc. Electrolysis of the zinc chloride to extract the zinc and recover the chlorine.

One of the chief merits of the process is that it is so perfectly cyclical. The chlorine merely goes round and round; the works takes in ore and electrical energy, and turns out metals, sulphur, and gangue. In treating sulphide ores with chlorine, as in analysis, or in the action of chlorine on sulphides generally, chloride of the metals and chloride of sulphur are produced. This is the reaction described in most text-books of chemistry. The formation of chloride of sulphur would be fatal to the process, however, as we should lose both the chlorine and the sulphur, and there is no convenient way of getting rid of large quantities of this offensive compound, far less of recovering the chlorine and sulphur. Decomposing with water is not a cyclic or a practical process.

The discovery that sulphide ores can be decomposed on the large scale by chlorine so as to give off sulphur and not its chloride, is, if we may say it with modesty, a possible turning-point affecting a vast realm of metallurgy.

The middle parts of the process, by which the mixed chlorides are converted into chloride of zinc by substitution and elimination of the other metals and of the gangue, involve ordinary chemical engineering only, though there is considerable room for ingenuity in inventing and working out the methods on a large scale.

The electrolysis of zinc chloride is supposed to be very difficult or impossible. We have overcome any difficulties. Zinc is chosen as the final metal to be separated from the chlorine for two reasons: because it is chemically easy to substitute it for all the metals we want to extract, as it is very electro-positive; and because it is easy to extract by electrolysis.

Smelting Lead Zinc Bluestone.

The actual process, as applied to some particular ore, may now be described. The Broken Hill slimes may be taken as a good example.

The crushed ore is run into a transformer. This looks like a small blast-furnace made of fire-clay with iron outside, or of lined iron. It runs continuously, and we may start our description at the stage when a tapping has just taken place. The transformer then contains about a hundredweight of fused chlorides and gangue. The gangue almost floats in the chlorides. If much lead is present much of the gangue floats, so there is no caking or silting up. The top of the transformer has a cone like a little blast-furnace. Ore is poured into the fused chlorides, and at the same time chlorine is blown in. The chlorine enters at the bottom by a sort of tuyere, which is a carbon tube. The cold part of this tube is connected to an iron pipe, which brings the chlorine. Dry cold chlorine is easy to handle. It does not touch metals, and iron can be used freely. The chlorine bubbling through the fused bath displaces the sulphur, which comes off and is condensed. The action of chlorine on the sulphides in question evolves a great deal of heat, so that the transformer is self-heating, and there is no coal or coke firing or outside heating of any sort. The temperature is controlled by the rate of

admission of chlorine. If the temperature is too low chlorine of sulphur may be formed. This may also be formed if there is a deficiency of ore supply. On the other hand, if the chlorine and ore are supplied too quickly, the transformer will get too hot, and some of the chlorides will distil over and be condensed with the sulphur. By running the transformer fast the temperature can be got so high that all the chlorides distil over, leaving only the gangue. The bulk of the transformer gives easy regulation.

The temperature is the main consideration in determining the size of the transformer. It must be of such a size that when running at its normal rate the heat is conducted through the lining and radiated from the surface at such a rate that the contents keep at the right temperature. There is considerable margin allowable in temperature, and the temperature is under control by regulating the flow of chlorine and of ore. The temperature can always be lowered by running in a little extra ore or reducing the chlorine; but the chlorine feed depends on the electrolytic vats, and is practically constant. The larger the transformer the longer it will preserve its temperature with any fluctuations of chlorine supply, and the cheaper the pumping, labour, &c. It is therefore best to have large transformers. We have so far used a ten-ton, but a larger size with thinner lining will probably be better.

The amount of gangue in the ore is important. As the gangue is about the same density as the chlorides, a large amount may be present without inconvenience as to fluidity. If it is of course an advantage to be able to work on ores with little metallic content. It is quite easy to work with the metallic contents only half the ore, or even less. Poorer ores can be made workable by addition of those with more metal. The temperature depends on the metals in the ore too. Thus blende heats much more than copper sulphide; so that, other things being equal, a copper ore with little zinc should be run through faster, or mixed with, say, a zinc-lead ore.

To return to the working of the transformer, it is started with the remains of the last charge, and then chlorine and ore supplied till it is full. The regulation needs no skill. A hole can be opened at the top of the transformer, and as it is connected through the sulphur chamber to a chimney there is a general suction. This draws air in at the hole, which burns the sulphur vapour. The blue flame shows there is enough ore. If too little is fed, fumes of ferric chloride fill the top of the transformer and pass into the sulphur. This is to be carefully avoided, and there should be excess of sulphides in the transformer until the end of the charge. At the end the ore feed is stopped, and the transformer run till brown fumes appear. These are bypassed round the sulphur chamber. The charge is then run out, and allowed to cool.

At first great difficulty was expected in pumping the chlorine, as a pressure of some ten to fifteen pounds on the inch is needed when the transformer is nearly full. The pumping presents no difficulty, and a chlorine pump will run day and night continuously without trouble. The well-known patented method with sulphuric acid flooded pumps would have been available; but such complications are quite unnecessary with dry chlorine. The dryness is of vital importance here.

We now come to the intermediate or chemical stage of the process. This varies with the ore used. We may take the Broken Hill slimes, and imagine there is copper too. This would be about as troublesome an ore as we could have. We have used the Broken Hill ore and mixed it with a Tasmanian copper ore, but we have chiefly worked on it alone. The fused mass from the transformer consists of chlorides of lead, zinc, iron, manganese, copper, silver, and gangue. It is run into water and through a filter-press when cool enough. This takes out the gangue and lead chloride, carrying most of the silver. The gangue is easily separated from the lead and silver chlorides, and these chlorides are then dried and fused in contact with lead, which extracts the silver and any gold; and then with zinc, which gives lead, practically pure, and

anhydrous neutral zinc chloride, which is ready for the electrolysis vats.

The filtrate from the press contains a little lead and silver in solution, and copper, iron, manganese, and zinc. The lead and silver are taken out with spongy copper. The copper is taken out as sponge or "cement" by zinc, and we have left iron, manganese, and zinc chlorides.

The iron is chlorinated up to the ferric state, and zinc oxide is added to cause precipitation. This throws down hydrated ferric oxide. This is the base of iron paint, and is marketable, its value depending on the colour obtained. The solution is further chlorinised in presence of more zinc oxide, and the manganese goes down as peroxide.

We have now substituted zinc for all the other metals in their chlorides, and have nothing left but zinc chloride. This is evaporated down carefully and fused. This decomposes some of the chloride, and makes an oxychloride. Steinhart evaporates *in vacuo* to produce neutral anhydrous zinc chloride. We have not done this; we find that with cautious boiling down there is not much oxygen in the final result. This is got rid of in open preliminary vats, which use inexpensive anodes, which are gradually used up. The consumption is less than if all the oxygen went off as monoxide. The anhydrous neutral chloride from these vats is then added to that from the lead chloride substitution, and is taken to the final electrolysis vats.

The electrolysis vats are internally heated, as in the case of aluminium. The cathode is fused zinc, and the anode is carbon. Some makes of carbon do not stand well, but suitable carbons serve to stand permanently. Of course chlorine has no action on the carbons. The vats are kept under a very light suction, so that if there are any leaks air goes in instead of chlorine coming out. The carbons are not hot enough to be burnt by this small admission of air. As the vats are kept warm by the excess of the electrical power over the chemical, the larger the cell the lower the electromotive force, so that if the cell were large enough we could get down nearly to the electromotive force corresponding to the heat of formation of zinc chloride at that temperature. So far 3000 ampères has been the current used, but this means a very small vat. The output of fused salt vats is enormous in comparison with aqueous work. A 10,000 vat is now being tried. Above that size the current will be inconvenient. With the small vats four volts per cell is needed, with 10,000 ampères three should do. It is best to count on four; this allowance ought to cover the power for the preliminary electrolysis too. The current efficiency is practically unity. Zinc smoke is of course formed if the temperature is too high.

The vats are very simple; merely iron cases lined with fire-brick. The chloride soaks into the porous brick and solidifies somewhere, so it is really a vat with zinc chloride walls.

Cost of Process.

As to costs of the process; the first thing to realise is that it smelts for all the metallic contents of the ore, not for only one. That all the metals are completely extracted. There is no waste by fumes or imperfect extraction, and there is no slag. The gangue looks like river sand. There is no room for loss. All that comes into the works is ore and electrical energy; all that goes out is pig-metal, sulphur, gangue, and oxides. The chlorine goes round and round. There is no room for appreciable waste of chlorine either. A leak that would show in the balance sheet would make the works uninhabitable. There is, however, a trace of chlorine in the iron oxide, as it is apt to contain a little oxychloride. There is also a loss in collecting the hydrochloric acid from the boiling down of the zinc chloride. A little chlorine must therefore be added to the stock. This can be done by buying crude zinc chloride, or galvanising pickle, or precipitating calcium chloride with zinc sulphate. In out of the way places it is much simplest to buy zinc chloride, as it is more portable than hydrochloric acid.

It may be said that a process for such a problem must

be a maze of chemical operations, and when you come to the end you have to begin again. This is not the case here at all. The process has only three simple stages:—(1) Transforming sulphides into metallic chlorides and sulphur; (2) substituting zinc for all the other metals in the metallic chlorides; (3) electrolysing out the zinc, and recovering the chlorine.

Compare this with ordinary metallurgy. To describe the metallurgy of a single metal at all adequately requires a book. Try and explain even most superficially the metallurgy and refining of argentiferous lead, zinc, and copper to any one quite new to the subject in the few pages here devoted to description, and it will be seen how simple the new process is. Add to the description of the metallurgy of these metals an account of the refining of copper and zinc, and refining and de-silverisation of lead, and even then you have only half done. To make the comparisons on all fours you must give an account of the concentration and separation of refractory ores, and give a description of methods for dealing with a mixed ore of lead, zinc, silver, iron, and copper. There can be no doubt that though the steps in the new process sound unfamiliar to ordinarily trained metallurgists, it is in comparison ludicrously simple. But there is even more than this; the new process treats ores, whose smelting by ordinary processes cannot be described, even with unlimited complications, because they are at present untreatable.

As to costs, everything depends on what ore is used, and where it is used.

The most obvious course is to work on refractory ores which are otherwise valueless, but leave large metal contents. The cost of the ore delivered at the works is then known. Thus even in England Blue-stone ore can be bought and delivered at from £2 10s. to £3 a ton, ready for running into the transformer. The metal content is £8 16s., taking zinc at £20, lead at £12, and silver at 2s. If higher prices can be maintained for pure metals, of course the content must be taken at a higher value. This figure includes all valuable contents.

The cost of the intermediate process is difficult to state, as it is a question of locality and labour. The capital in this part of the process is small, but in the estimates heavy allowance has been made for deterioration, and all other contingencies. On the other hand, the conversion, which alone is a new sort of chemical experience, is extremely simple and easy. The intermediate processes depend on the ore. Thus, if there is no copper, part is cut out altogether. If there is no iron, by which I mean not even enough to hurt the zinc, the transformer product would not be dealt with in the wet way at all. The wet way is to get rid of iron and manganese, and to get out copper. Lead and silver can be got out by substitution in the fused state with great ease, but copper has too high a melting-point, and is therefore taken out by the wet process.

To make a very safe shot, the cost of all the process except the energy for electrolysis may be taken at a rough figure of 30s. per ton of ore. This will easily cover all depreciation, a small percentage on capital, all labour and management. As the process uses ores with about half the contents metallic, though it can work with half sulphides, this means about 30s. per ton of chloride of zinc handled. Most of this work is pure circulation, agitation, and filtration, all cheap processes. The solution is not bulky, as it is used as strong as the filter-press cloths will stand. Evaporating down and preliminary electrolysis are the most expensive parts of the process, and they are not serious. The loss of chlorine, which has not yet been determined, may be taken as costing about 1s. a ton of ore for every 1 per cent of chlorine wasted, if it is made up by buying chloride of zinc. If it is made up by hydrochloric acid or calcium chloride, which is far cheaper where there is no carriage difficulty, the cost is about half that of zinc chloride. This loss of chlorine is included in the 30s. a ton of ore, and in the estimates to follow, as power is taken at prices in England where it is not cheap, we may assume we can get calcium chloride cheap. This does not

complicate the estimate by showing a zinc output a little higher than the intake in the ore.

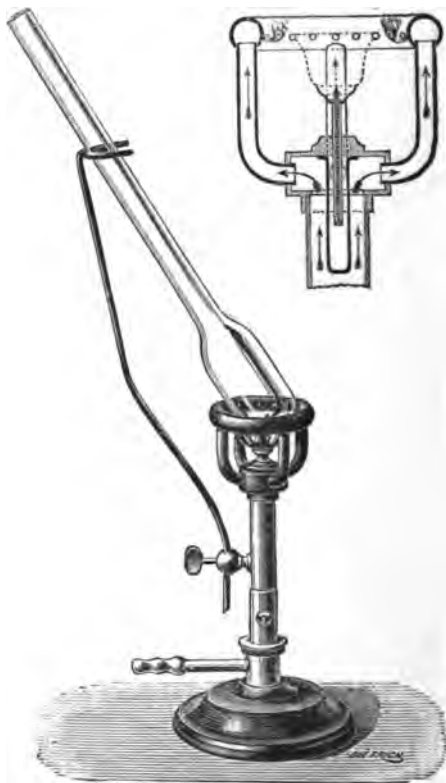
The cost of energy is very easily determined. If it is generated by steam-engines of high grade in this country in a convenient district, it may be taken as 0·25 per kilowatt-hour, including depreciation, coal, oil, repairs, labour, and management, and a small interest on capital. This is a close estimate, but one which can be realised on large plants running day and night on uniform full loads. The cost by producer gas and gas-engines is somewhat uncertain; it may be taken at 0·125, though that is probably a very tight figure. Water-power in a favourable situation may be taken at 0·085. This refers to water-powers such as on the way down from the American lakes to the sea. It is for a works planted close to the generators, and does not cover rotary transformers, or step-down plant.

(To be continued).

A NEW GAS-BURNER.

By L. QUENNESSEN.

In the present method adopted for the assay of gold, silver, and platinum, after having cupelled to get rid of the oxidisable metals, the cornets are attacked with boiling nitric or sulphuric acids, and we meet with several difficulties during the operations in which the liquids are heated over Bunsen burners modified by Debray.



1. In the assay of gold and silver we boil the cornet first with nitric acid of 1·18 density, then, after decantation, with acid of 1·286 density.

In this operation the boiling does not go well; to regulate it we are obliged to put a fragment of porous charcoal into the matras, obtained by calcining vetch seeds in a closed vessel.

Then, when the gold is present in very small quantities compared with the silver, especially when the alloy contains less than two-thousandths of gold, the latter becomes divided into a very fine powder as the silver gradually dissolves, and by attaching itself to the sides of the vessel causes bumping, which may lead to losses by projection.

2. In assays of platinum and gold, in which it is necessary to dissolve the inquartation silver in concentrated boiling sulphuric acid, bumping also occurs on boiling the liquid, and this frequently leads to the breaking of the matras.

The new burner (which is shown in the accompanying illustration) obviates these drawbacks. The gas comes out through holes arranged round the interior of a crown, so that the heating is annular and the boiling is effected, no longer at the bottom, but round the sides of the matras. Thus projections are prevented. Further, according to the use for which this burner is intended, it is necessary that the heat can be applied at various heights. To effect this, the bottom of the matras is held by a copper support in the form of a tulip; this latter is brazed to the upper part of a screw that can be turned up or down the axis of the heating crown; the end of this screw fits into a tube to prevent all loss of gas.

In assays of gold, it is no longer necessary to use grains of carbon, the use of which was often very inconvenient.

In assays of platinum, the parting with sulphuric acid, which can be boiled in from five to seven minutes, is effected with the greatest ease.

This burner can be used also in the estimation of nitrogen by Kjeldahl's process; this process is, in fact, much easier to carry out in assay matrasses on account of the length of their necks, which is much greater than that of the necks of flasks, even of the same capacity, generally used in chemical work.

A CHEAP AND EFFICIENT WATER-BLAST.

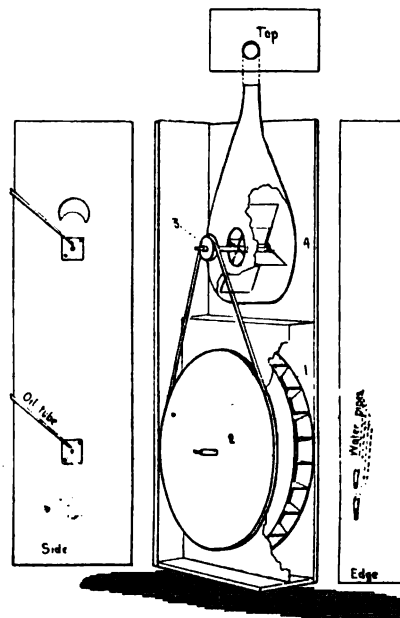
By FRANK L. HANN.

THE work performed in the chemical laboratory of Cornell College emphasised the necessity of a water-blast, and some of the well-known kinds were purchased. The laboratory is situated on the third floor of the building, where the water-pressure was found to be scarcely 30 pounds to the square inch. This was insufficient to maintain the blasts satisfactorily. It was therefore necessary to set about to devise a blast which would be suitable where the water-pressure is low, and which would give good results with a small jet of water. The apparatus here described has been in use for six months, and seems fully to meet the conditions.

Experiments with various devices were made, but the one that has given the most satisfactory results consists of a small water-wheel (1), a large pulley-wheel (2), connected by belt with a small one (3) for driving a fan-wheel (4), all of which are enclosed in a rectangular wooden box, 7 x 12 x 24 inches.

The water-wheel is 9.5 inches in diameter and 1.5 inches thick, and is made of galvanised iron. Its construction is something on the plan of an undershot wheel. There are twelve paddles on the rim, projecting an inch, against which the water strikes to produce the motion. Each paddle is placed in line with a radius of the wheel. The larger pulley-wheel has a diameter of 10 inches, is of a good quality of white pine, and was soaked for three hours in melted paraffin to prevent warping. It has a groove $\frac{1}{8}$ -inch in diameter for the belt. These wheels are mounted on a $\frac{1}{8}$ -inch shaft, turned down at each extremity to $\frac{1}{16}$ -inch bearing. The smaller pulley-wheel is of wood, $\frac{3}{4}$ of an inch in diameter, with flanges $\frac{1}{4}$ of an inch deep. The fan-wheel consists of four wooden paddles and is 6 inches in diameter. This wheel and the smaller pulley are mounted on a $\frac{1}{8}$ -inch shaft, which is likewise turned down

to $\frac{1}{8}$ -inch journals. The boxings in which the journals run are simply pieces of iron, $\frac{1}{8}$ of an inch in thickness, with holes drilled to fit the journals, and the iron pieces are fastened to the inside of the case. The water-wheel is separated from the rest of the apparatus by an air-tight tin partition to confine the water, which is conveyed to this wheel by two tubes consisting of mouth blowpipes cut off at the small extremity to attain an inside diameter of $\frac{1}{8}$ of an inch. These are placed through the edge of the case in such a way that the water from one strikes the paddles just a little below the axis, at an angle of 45 degrees to the horizontal plane of this axis, and from the other lower down and nearly parallel to this plane. The maximum effect is



attained when the stream strikes the centre of the paddle when the paddle is exactly at a right angle with the stream. Ordinarily it has been found necessary to employ only one stream of water. Ample provision must be made for the escape of the waste water. The fan is enclosed in a galvanised iron compartment, and somewhat resembles the tube with an inside diameter of $\frac{1}{8}$ -inch. By attaching fan used by the blacksmith. It should have an outlet air a Y-tube to this, two blasts can be used as easily as one. A thick-walled rubber tube about $\frac{1}{4}$ -inch in diameter has proved to be the most effective belt. The bearings must obviously be kept well lubricated to secure easy action.

Chemical Laboratory, Cornell College.

The Autoxidation of the Hydrocarbides from Coal-tar.—Max Weger.—The author has examined the modifications which take place on keeping these hydrocarbides purified in such a manner that they do not become coloured on contact with sulphuric acid. The experiments were carried out on trimethylbenzene, hydrindene, and tetrahydronaphthalene. After fifteen months all these products had become more or less changed, no matter how they had been kept, whether in ground-glass stoppered bottles, in sealed tubes, or in tubes simply closed with plugs of cotton-wool, either in the dark or exposed to sunlight. The specimens exposed to air and light are the ones that change the most; the phenomenon seems to be one of autoxidation, with the formation of acids.—*Berichte*, vol. xxxvi., p. 309.

THE MAZZA SEPARATOR FOR GASES.*

By Capt. VITTORIO CALZAVARA,
Technical Manager of the Società Civile Veneta per l'Industria del
Gas ed Elettricità, Editor of the Monthly Technical Review *Il Gas*.

THE applications of centrifugal force for the separation of liquid substances forming a compound mixture have, for some time, made their way in the industrial world, and many apparatus are based on this principle, as, for instance, the *Alpha* milk-skimmers. But, up to quite recently, it was not deemed possible that centrifugal force could succeed in separating gaseous molecules composing a mixture, and in grouping the same in strata, varying according to their density.

Signor Edoardo Natale Mazza, formerly an officer in the Royal Engineers of the Italian Army, has solved the problem. After having surmounted many obstacles, and conquered much diffidence, Signor Mazza has succeeded in demonstrating practically, that by means of his Separator gas molecules of different density, united in a mixture, are separated and grouped together in concentric strata by the action of centrifugal force.

The Separator is a very simple machine, by means of which, and with the sole action of centrifugal force—therefore *mechanically*—the various components of gaseous mixtures are separated. This machine, as is shown by a drawing, consists essentially of a drum, revolving with great velocity, and into which the gaseous mixture to be treated is sucked in, in consequence of the rotation; the components, divided by the different effects produced on them by the centrifugal force, according to their various densities, escape by different outlets, and are forced by the same separating energy to follow their various destinations.

The separation of the gaseous elements takes place with greater or lesser facility, according to the greater or lesser difference in density of the components of the gaseous mixture; but in every case the result obtained is most noteworthy, even when the difference in density is small. In fact, atmospheric air which, as is known, is composed of oxygen and nitrogen, that is to say, of elements the density of which differs but slightly, centrifugated by the Mazza Separator has yielded at the periphery a quantity of air so far enriched in oxygen as to serve regularly to improve the fuel of the steam-boiler grates.

We have precise data as to the regular working, during several months, of the Separator, as for instance at the works of Hofmann and Co., Turin, where, according to the certificate delivered by this firm, the coal consumed by them has shown an average economy of 16 per cent, as against the consumption of fuel for the same boilers without the apparatus; at the paper manufactory of Messrs. Sezzano, at Bettola Sesia, where the saving has reached 22 per cent; and at the Turin Glue and Manure Co.'s works, where during three months working with the Separator, an increase in the yield of fuel attained 23 per cent.

Before the apparatus entered the industrial world, it had been the object of technical study and experiments; Mr. Robert P. Bethell, C.E., of Jarrow, England, the Società Italiana del Gas, in Turin, Prof. Benedetto Porro, of Turin, Prof. Dr. Schaefer, of Charlottenburg, besides others, after having made experiments at different places, at various epochs, and under different circumstances, each and all obtained such results as to enable them to testify to the success of the Separator, and to deliver precise and explicit declarations.

The Imperial German Patent Office granted Signor Mazza letters patent on the strength of Prof. Schaefer's report, and we consider it interesting to quote the words with which his report terminates:—

"It is the first time that, by means of Signor Mazza's invention, one has really succeeded in applying the known process of centrifugal force to gases with the result, up to

now unforeseeable, that even with a moderate velocity of rotation, the quantity of oxygen in the atmosphere is increased at the periphery. The problem is thus in principle solved, and results have been obtained which are worthy of note, both from a scientific and a technical point of view."

Mr. Robert P. Bethell has certified:—"That the experiments prove conclusively that the machine is capable of increasing the amount of carbonic acid, sulphuretted hydrogen, and oxygen gases at the top outlet, such being the claims put forward by the patentee."

From a purely chemical standpoint, the results of the Separator have likewise been confirmed, and we may quote what Prof. Porro, who has made a great number of analyses of air centrifugated with the apparatus, wrote to Signor Mazza on the 18th of July, 1902:—

"Having already made a great number of analyses, I have become intimately convinced that your apparatus serves to centrifugate and to separate gases, and that the components of atmospheric air likewise undergo this physical law of centrifugation, and that the air is sensibly enriched with oxygen at the periphery of the apparatus to such an extent as to give good practical results."

Another ascertainment of special value, and particularly worth mentioning, is the report of the special Commission appointed by the Ministry of Marine of the Kingdom of Italy, to investigate and report on the practical results of Signor Mazza's apparatus. This Commission, after having made experiments under the severest control and the most careful surveyance, ascertained the following three very important results:—

1. That by using air centrifugated by the Mazza apparatus at a pressure of 4—5 atmospheres, 1 kilogram of New Peltan Main evaporated 12—15 kilograms of water.

2. That the quantity of ashes and cinders was *one-half* that of the same fuel when ordinary air was used.

3. That during the experiments, the temperature of the products of combustion, shortly before leaving the discharge outlets, was higher by 16° than the temperature which is to be ascertained in combustion under ordinary circumstances.

In consequence of this report, the Royal Ministry gave the order for an apparatus destined for the Taranto Arsenal.

Considering, however, that the industries, the representatives of which have met here, are of a special kind, we shall occupy ourselves more particularly with the applications of the Separator to the gas industry, after having made some brief general remarks.

Centrifugal force applied to industrial gaseous mixture, such as lighting-gas, water-gas, &c., becomes perceptibly manifest at an angular velocity of 300 revolutions per minute, with a radius of rotation of 40 c.m., provided the mechanical action does not last less than thirty minutes. By increasing the angular velocity, one can reduce the time of subjection to centrifugal force, without however, going below twenty minutes; thus, with this element of time, and with the angular velocity carried up to 1000 revolutions per minute ($r=0.40$), the best results are obtained in separating the above-mentioned components of industrial gases.

In centrifugating lighting-gas, one must bear in mind that a too energetic centrifugal action seems to exercise a certain influence on the composition of some of the richer carburets, or, rather, it seems to alter their illuminating power; we would therefore advise, as more convenient for industrial purposes, in this special case, the centrifugal force, resulting from the formula—

$$\frac{25 \cdot 9}{0.40} = \frac{V}{r} = F.$$

Another remark to be made is that concerning the special affinity manifested by some gases, and not justified either by the force of diffusion, or the force of gravity, which is precisely that which produces the phenomena of centrifugal force. In fact, by mixing on the one hand, in

* Memoir presented at the Congress of the Deutscher Verein von Gas- und Wasserfachmännern, Zurich, June, 1903.

equal proportions, carbonic acid, oxygen, and nitrogen, and on the other, carbonic acid, carbonic oxide, and nitrogen, and applying the action of centrifugal force in identical conditions, the CO_2 of the second mixture separates with greater difficulty than that of the first mixture, whereas the difference in density should be more sensible in the second mixture, CO being, as is known, less dense than O. It would appear from this that a special affinity causes the molecules of CO and those of CO_2 to commix.

With regard to these, and other special affinities to be encountered, we may mention the force of diffusion of molecules or molecular velocity, which has often been put forth as an insurmountable obstacle to the solution of the problem of dividing the components of given gaseous mixtures *mechanically*.

First of all, we must bear in mind that the force of diffusion, or the impulsion of molecular velocity, takes place in every direction, and with the same intensity, presenting, therefore, as a geometrical place of action, a sphere. Now, if a given molecule thus moved is considered as also subject to a new force, acting, however, in a determined direction, there will evidently be a tendency towards a displacement of what results from the sole impulsions due to the force of diffusion. We get an idea, however rough, of this by observing the mode of acting, as well as the phenomena of rarefaction and compression which centrifugal ventilators present; but this is even better shown by the phenomenon, often noted, of gas mixtures of divers densities, as, for instance, water-gas, which, left for some time to rest in the gasometer, gets *stratified* to a most perceptible extent, in accordance with the law of gravity.

(To be continued).

NOTICES OF BOOKS

Thirty-ninth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1902. London: Eyre and Spottiswoode. 1903. Pp. 193.

THE number of works now registered under the Acts in England, Ireland, and Wales is 1044. Of these, 75 only are works decomposing salt, while the remainder, 969, carry on processes which are scheduled under the Acts of 1881 and 1882. These numbers show a reduction of 8 alkali works, and an increase of 16 scheduled works in 1902. There are also 124 works registered in Scotland, bringing the total number of works registered in the United Kingdom to 1168. There were 4946 visits to works, and 5091 tests made during the past year, and it is very satisfactory to observe that no proceedings have been entered during the year for recovery of penalties for the infraction of limit clauses under the Act of 1881, or for failure to use the best practicable means for the prevention of the escape of noxious and offensive gases.

The Chief Inspector regrets that he has to report year by year, that success has not followed the various proposals made for reducing the acid escapes from the exits of the Chance-Claus process. He has, however, every reason to hope that experiments now in progress to reduce the escape of acid gases will turn out to be successful; before many months have elapsed all the data should be worked out, and he trusts that by then all the difficulties, of which up to now surprisingly few have presented themselves for solution, will be overcome.

The average escape of acids of sulphur and nitrogen from exits of sulphuric acid works, in which this manufacture is carried on by the lead-chamber process, is still maintained at a most satisfactory level, indicating the constant care and attention that are devoted to the conduct of this manufacture. The average escape from the 209 exits tested varies but slightly from the figures already given for 1900 and 1901.

Through the courtesy of manufacturers, the Chief Inspector is enabled again to give the figures showing the production of ammonia from all sources in the United Kingdom. These figures show a steady increase year by year, the most important contributor being, of course, the gas industry.

With regard to salt works, the limit escape of hydrochloric acid allowed is one-fifth of a grain per cubic foot of escaping gases; the average escape slightly exceeds one-fourth of this.

The conditions of trade have not been conducive to the renewal of activity of arsenic works in Devon and Cornwall, but the escapes of arsenic from this class of works have, on the whole, been low, and the works themselves maintained in satisfactory condition.

Tar works remain by far the most widely spread process whose supervision was added to the inspecting staff by the Act of 1892; the number of works remaining, as in last year, at 128. No modification of importance in the processes employed during the year calls for any comment.

CORRESPONDENCE.

THE SCIENTIFIC IMAGINATION.

To the Editor of the Chemical News.

SIR,—In the recent newspaper discussion of the hypothesis of Sir William Crookes, Sir Oliver Lodge, and others, concerning the constitution of matter, I have been quoted occasionally as a somewhat scornful opponent of the new ideas. Since these reports by no means represent the subject in a true light, I venture to write this letter in order to correct the misunderstanding.

A quotation from Sir William Crookes's article, which is now accessible to all, in the issue of *Science* for June 26th (see CHEMICAL NEWS, vol. xxxvii., p. 281), will perhaps most easily clarify the case. He says:—

"Indulging in a 'scientific use of the imagination,' and pushing the hypothesis of the electronic constitution of matter to what I believe to be its logical limit, we may be, in fact, witnessing a spontaneous dissociation of radium, and we begin to doubt the permanent stability of matter."

It must never be forgotten that theories are only useful so long as they admit of the harmonious correlation of facts into a reasonable system. . . . Are we not incessantly learning the lesson that our researches have only a provisional value? A hundred years hence, shall we acquiesce in the resolution of the material universe into a swarm of rushing electrons?"

The conditional statement and frank interrogation, appearing in this final climax of his, place him in a very different position from that to be inferred from the daily papers. Here is no claim to a great discovery, but merely the statement of the possible consequence of pushing an avowedly hypothetical inference to its logical extreme, with full recognition of the likelihood of its fallibility. With such an attitude no reasonable person can quarrel. The hypothesis that the hypothetical atom is divisible—and this is the particular proposal which has caused so much excitement—is, indeed, not unreasonable: but it is not the only possible explanation of the facts. In view of this circumstance, and also of the very recent discovery and the surprising nature of some of the phenomena concerning radium and the Röntgen rays, it seems to me premature to own unswerving allegiance to any definite interpretation at present.

The popular discussion of this question, as of so many scientific questions, has been much confused by the inability of many writers to distinguish between fact and hypothesis; and it was against this confusion that I argued in the interview which led to the exaggerated report. Facts are determined by observation and experi-

ment, and their truth depends only upon the accuracy of the observation and experiment. Their discovery is a lasting addition to the knowledge of mankind. On the other hand, hypotheses are attempts to interpret the facts; and many hypotheses, from their very nature, can never be proved. Although usually transitory, they are often very useful in suggesting further experimentation; but they become dangerous when mistaken for realities. Faraday, one of the greatest of scientific discoverers, dreamt many such scientific dreams; they were his leading inspiration, and they never harmed his work, because he always recognised their true place. In the same way, these new inferences concerning the reasons of the remarkable behaviour of radium may be highly suggestive and therefore valuable, if their inevitable limitations are always borne in mind.—I am, &c.,

THEODORE WILLIAM RICHARDS.

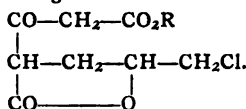
Peterboro', N.H., July 2nd, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 1, July 6, 1903.

New Syntheses effected by means of Molecules containing the Methylene Group associated with one or two Negative Radicles. Action of Epichlorhydrine on Sodium Acetonedicarboxylic Ethers.—A. Haller and F. March.—In a previous research the authors show that, amongst the products of the reaction of epichlorhydrine on the acetonedicarbonates of methyl and ethyl, compounds can be isolated having the formula—



These substances are of the nature of chlorated ketoacetones and ether salts, which give with semicarbazide perfectly crystallised compounds. The authors now continue their researches on these complex molecules, and succeed in etherifying them by opening the lactic chain. The new compound thus obtained gives no precipitate with copper acetate, and does not combine with semicarbazide. These facts show that the ketonic function has disappeared, and that the complex $\text{—CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{R}$ has been modified.

Simplification of the Analysis of Silicates by the Use of Formic Acid.—A. Leclerc.—The separations made during the analysis of silicates have long been known to be incomplete. The author finds that the difficulties arise from the acid employed for the solution of the silicate and for the formation of basic salts. The molecular weight of the acid is of great importance, and nitric acid—though of low molecular weight—is not so low as that of formic, the latter being therefore preferable in these analyses.

Conditions of Production and Stability of Hyposulphurous Acid.—J. Aloy.—Hyposulphurous acid can be rapidly produced by the action of an alcoholic solution of sulphurous acid gas on sulphur. The presence of alcohol and of neutral salts increases the stability of hyposulphurous acid, whilst the presence of acids and the action of solar light aids its decomposition. The mode of decomposition of the acid depends on the proportion of sulphurous acid existing in the solution.

Etherification of Hydracids.—A. Villiers.—When a mixture of hydracids and alcohol attains an equilibrium corresponding to a definite temperature, and is then allowed to cool, various modifications take place. The slowness

with which these variations are produced, and that with which hydrochloric acid is etherified, does not allow of a complete investigation of this matter, but the results actually obtained by the author show the direction in which the reaction is tending.

Dibrom-acetylene. Purification; Cyroscopic Analysis.—P. Lemoult.—By the action of alcoholic potash on $\text{CHBr}=\text{CBr}_2$ and fractionation at the moment of preparation, pure dibrom-acetylene is obtained, of which the molecular complexity and the position of the bromine corresponds to the formula $\text{CBr} \equiv \text{CBr}$. The author proposes to continue his researches on this subject.

Lactose.—Em. Bourquelot and H. Hérissé.—Lactose accompanying emulsine, emulsine without lactose, and finally lactose without emulsine, are found in certain plants. All these facts are in agreement with the hypothesis of the individuality of the two ferments.

Action of Sodium on Carbon Tetrachloride and Chlorated Benzene. Formation of Triphenylmethane and Hexaphenylethane.—Jules Schmidlin.—Tetraphenylmethane is a hydrocarbon of a very simple structure, and of great stability, judged from its chemical and thermo-chemical properties. It cannot be obtained by one of the simple methods used for the synthesis of hydrocarbons. The action of aluminium chloride on benzene and carbon tetrachloride gives only triphenylmethane. Carbon tetrachloride and chlorated benzene treated with sodium give diphenyl, and a mixture of hydrocarbons, amongst which the author isolated and identified triphenylmethane and hexaphenylethane in small quantities.

Preparation of Primary Alcohols by means of the corresponding Acids.—L. Bouveault and G. Blanc.—The authors generalise the method of reduction described in a recent paper (*Comptes Rendus*, vol. cxxxvi., p. 1676). The method applies as well to acids of small molecular weight as to those higher in the series, but, in these cases, as in the last research, serious experimental difficulties have to be overcome. The ethers of benzoic acid and of its homologues with carboxyl substituted in the radicle, are up to the present time the only ones with which the reduction does not take place.

β -Cyclohexanediol-1,2-ethylene Oxide and its Derivatives.—Leon Brunel.—During the preparation of β -orthocyclohexanediol there is a transitory formation of an ether oxide. The author examines this ether oxide and finds on analysis that it possesses the formula $\text{C}_6\text{H}_{10}=\text{O}$. He also prepares certain compounds of this ether oxide, formed by the action of hydrogen, water, and sodium bisulphite on it.

Heat of Neutralisation of Hydroferrocyanic Acid. Heat of Formation of its compounds with Ether and Acetone.—MM. Chrétien and Guinchant.—Hydroferrocyanic acid absorbs vapours of different organic compounds, such as ether, acetone, ethylene oxide, epichlorhydrine, and allylic alcohol. The authors determine the heats of formation of compounds of this acid with ether and with acetone, by decomposing them with dilute potash in a calorimeter. They find that the compound of a molecule of solid hydroferrocyanic acid, with ether vapour, evolves 11 calories for each molecule of ether fixed, and with acetone vapour, 9.7 calories per molecule of acetone fixed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 4.

The Constitution of the Electrolytic Peroxides of Lead, Nickel, and Bismuth.—A. Hollard.—Already inserted in full.

A so-called Electrolytic Reduction of Chlorate of Potassium.—André Brochet.—A controversial paper in which the author criticises the results published by Mr. C. R. Burrows and Prof. Bancroft, on a process for the electrolytic reduction of chlorate of potassium.

The Oxalomolybdates.—G. Bailhache. — Already noticed.

The Solubility of Gypsum in Solutions of Sea-salt.—Ch. Cloëz.—The author has obtained the following results in his experiments on the solubility of gypsum in solutions of sea-salt :—

Weight of NaCl in 100 c.c. of water.	Weight of gypsum dissolved.
Grms.	Grms.
0.0	0.2
2.44	0.635
4.77	0.826
9.50	1.056
14.22	1.193
23.15	1.275
31.3	1.583

Thus the solubility of gypsum in solutions of chloride of sodium increases in a regular manner with the concentration of these solutions. The determinations were made at a temperature of 14° on solutions remaining in contact for three months with an excess of pure hydrated sulphate of lime, the solutions being stirred up every day.

Experiments on Plaster-of-Paris; Baking the Gypsum.—Ch. Cloëz.—It was found by experiment that anhydrous plaster-of-Paris absorbs moisture when exposed to the air :—

In 1 hour it absorbs	3.70 per cent of water
" 2 hours "	4.27 " "
" 3½ " "	5.70 " "
" 19 " "	7.57 " "
" 27 " "	7.77 " "
" 74 " "	7.93 " "

The above experiments were carried out at 14—16°. At a lower temperature the absorption takes place more slowly, but it reaches the same limit. Anhydrous plaster, which is very easy to prepare, is an excellent dehydrating material, by which means alcohol can be brought easily from 90° to 98°.

MISCELLANEOUS.

Australasian Association for the Advancement of Science.—The tenth meeting of this Association will be held at Dunedin, N.Z., from the 6th to the 13th January, 1904, under the presidency of Prof. T. W. E. David, M.A., of the Sydney University. The chairman of the local council will be the Right Rev. Dr. Nevill, Bishop of Dunedin. The presidents of the various sections will be as follows :—A., Astronomy, Mathematics, Physics, and Mechanics—Prof. W. H. Bragg, M.A.; B., Chemistry—J. Brownlie Henderson; C., Geology and Mineralogy—W. H. Twelvetees, F.C.S.; D., Biology—Col. W. V. Legge, R.A.; E., Geography—Prof. J. W. Gregory, D.Sc., F.R.S.; F., Anthropology and Philology—A. W. Howitt, F.G.S.; G., Social and Statistical Science—(not yet filled); H., Agriculture—J. D. Towar; I., Architecture, Engineering, and Mining—H. Dease, M.A., M.Inst.C.E.; L., Sanitary Science and Hygiene—Dr. Frank Tidswell; and J., Mental Science and Education—John Shirley, B.Sc. In addition to the meetings of the sections, arrangements are in progress for various entertainments, and for excursions to places of interest in the neighbourhood of Dunedin and to other parts of the colony. Further particulars can be obtained from the Hon. Local Secretary, Geo. M. Thomson, 129, Moray Place West, Dunedin, N.Z.

Institute of Chemistry.—July Examinations, 1903.—Examiners in Chemistry—Walter William Fisher, M.A. (Oxon.), F.I.C.; Prof. William Palmer Wynne, D.Sc. (Lond.), F.R.S., F.I.C. Examiner in Therapeutics, Pharmacology, and Microscopy—Arthur Pearson Luff, M.D. (Lond.), B.Sc. (Lond.), F.R.C.P., F.I.C. The following Candidates passed :—

Intermediate Examination.—James Alexander, Glasgow and West of Scotland Technical College; David Allam, Glasgow and West of Scotland Technical College; Harold Frederick Barke, Owens College, Manchester; James William Brisbane, King's College, London; John Alexander Campbell, Glasgow and West of Scotland Technical College; Arthur Charles Carter, University College, London; Reginald William Lane Clarke, Finsbury Technical College, London; Bertie James Eaton, Finsbury Technical College, London; James Dick Fraser, Glasgow and West of Scotland Technical College; James Stuart Hills, King's College, London, and the School of the Pharmaceutical Society, London; Leonhardt Erich Hinkel, King's College, London; Charles Edgar Male, King's College, London, and the School of the Pharmaceutical Society, London; James Miller, Yorkshire College, Leeds, and under W. McD. Mackay, F.I.C.; Russell George Pelly, Finsbury Technical College, London; Louis John Ezeziel Riley, Glasgow and West of Scotland Technical College, and the University, Edinburgh; Walter Charles Scott, Finsbury Technical College, London; David Spence, Glasgow and West of Scotland Technical College.

Final Examination for the Associateship (A.I.C.).—Branch "A" (Mineral Chemistry).—Alfred Vincent Elsdon, University College, London; Leo Frank Guttman, Ph.D. (Heidelberg), A.C.G.I., Central Technical College, London, and the University, Heidelberg; James Stewart Kerr, Assoc.R.C.Sc. (Lond.), Royal College of Science, London; Harold George Lacell, Assoc.R.C.Sc. (Lond.), Royal College of Science, London; Frederick Peacock Leach, Assoc.R.C.Sc. (Lond.), Royal College of Science, London; Henry Stanley Raper, B.Sc. (Vict.), Yorkshire College, Leeds; Ewing Smith, Glasgow and West of Scotland Technical College; George Steedman, Glasgow and West of Scotland Technical College. Branch "B" (Metallurgical Chemistry).—William Harold Keys, Birmingham University. Branch "D" (Organic Chemistry).—Walter Geoffrey Black, A.C.G.I., Central Technical College, London; James William George Brooker, Finsbury Technical College, London; Hamilton McCombie, M.A. (Aberdeen), Assoc.R.C.Sc. (Lond.), Aberdeen University, and the Royal College of Science, London; Sidney Scrivener Napper, A.C.G.I., Central Technical College, London; George Tattersall, B.Sc. (Lond.), University College, Nottingham; Henry Lucas Wall, Finsbury Technical College, London. Branch "E" (Analysis of Food and Drugs, and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy).—John Frederick Percival Fielding, King's College, London; Harold Adams Scruton, B.Sc. (Lond.), Yorkshire College, Leeds; Thomas Edward Wallis, B.Sc. (Lond.), School of the Pharmaceutical Society, London.

For the Fellowship (F.I.C.).—John Don, M.A. (Aberdeen), B.Sc. (Lond.), Aberdeen University.

Nerol: A New Alcohol found in Essential Oils.—H. von Soden and O. Zeitschel.—Nerol is a new terpenic alcohol resembling geraniol, and forming part of various essences. To isolate it, the essence is saponified in the cold with alcoholic potash; the oil remaining is washed with water and distilled in vacuo; two fractions are obtained, one of linalol and terpenes, and the other of terpineol, geraniol, and nerol. These two latter alcohols are transformed into acid-phthalic ethers, which are isolated and then saponified; in this manner we obtain a mixture of geraniol and nerol, which can be separated by adding powdered chloride of calcium, and washing with petroleum ether; geraniol gives an insoluble solid compound with chloride of calcium. The nerol passes into the petroleum ether, which is distilled, washed, and rectified. The return is 2 per cent. Nerol is a liquid having the composition $C_{10}H_{18}O$; its boiling point is 225—227°, and its density at 15° is 0.880; it has an odour of roses, much fresher than that of geraniol. Its acetate boils at 134° under 25 m.m., and its density at 15° is 0.917; the formate boils at 119—121° under 25 m.m.—*Berichte*, vol. xxxvi, p. 265.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation,"
London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and
Fermentation," London and New York (Macmillan and Co.), 1900.

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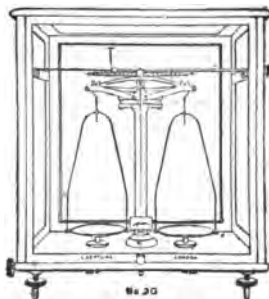
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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2281.

THE ACTION OF SALTS OF RADIUM UPON GLOBULINS.

By W. B. HARDY.

Two solutions of globulin from ox serum were used, one electro-positive, made by adding acetic acid, the other electro-negative, made by adding ammonia.

They were exposed in shallow cells, one wall of which was made of thin mica, to the radiations from 50 m.grms. of pure radium bromide, enclosed in a capsule covered with mica, so that two sheets of mica were interposed between the radium and the solution. No action took place in one hour.

The globulin was then exposed as naked drops, separated by 3 m.m. of air from the radium salt, with suitable controls, shielded from the radium.

In the solution the opalescence rapidly diminished—that is to say, solution became more complete. The solution was turned to a jelly, at first transparent, rapidly becoming opaque. The action was complete in about three minutes.

Radium, like other radio-active bodies, gives off matter in three states—(1) an emanation having the mobility of a heavy gas, (2) positively charged particles of little penetrating power, and relatively large size, (3) ultramaterial negatively charged particles, of a size much smaller than atoms. A mica plate will screen off 1 and 2, therefore the globulin solutions are unaffected by the ultramaterial negative particles. The rate of action and conditions of the experiment make it unlikely that the emanation was the active agent, though, owing to its nature, intense solvent or coagulating power may safely be predicated of it. The action observed was almost certainly due to the + particles. These are of material dimensions.

Globulin systems therefore seem to be completely transparent to the ultramaterial electrons, and so too, probably, are the living tissues, since the physiological influences of the discharges from radium seem to be limited to a superficial layer a few m.m. deep.

The experiments were carried out by the kindness of Sir William Crookes in his laboratory, and with his assistance. —*Proceedings of the Physiological Society*, May 16th, 1903.

CHLORINE SMELTING, WITH ELECTROLYSIS.*

By JAMES SWINBURNE.

(Concluded from p. 66).

Capital Cost.

As regards capital cost, it is difficult to say how much the plant for any particular case will cost, as it depends on the ores to be smelted and local conditions. It is therefore wise to allow a large margin on all the plant of a new description, and a large margin is left in the 30s. a ton for depreciation, repairs, &c.

The electrical generating plant is a different matter, however. A large installation may be taken at an outside figure of £25 per kilowatt, including buildings and spares. In this case, there is no accidental overloading, as in light and power distribution stations, so that £25 a kilowatt includes spares by overloading and separate plant.

It will be evident that the cost of generating plant is a consideration in the capital expenditure. In the case of water power at 0.086, the capital expense is borne wholly

by the owners of the power station. The power is there, and if it is not used for one purpose, it is used for another, so that the water-power company really takes no special risks involved in a new process. The 0.086 thus covers the capital of the water station, and no water-power capital figures in the process accounts. A given amount of available capital thus gives much better results on a water power.

In the case of a gas plant, the owners of the process may put up their own plant.

The capital cost of gas generating plants may perhaps be safely taken as £25 a kilowatt, but it must be borne in mind that there is more uncertainty about it, and more chance of its becoming antiquated soon. Improvements in gas generators and engines are more rapid than in steam just now.

In the case of steam generating plant, the same considerations come in. If the owners of the process put down their own plant, they must allow for high profits on a share of it. Though 0.25 is given as the cost of steam-generated electrical energy, that is only if there is no risk. No business men would put down a generating plant specially to supply us with nothing but a guarantee of 0.25 per kilowatt hour for a year or two. The nearest approach to such a case is a power station such as those being put up in various districts now. Even one of them would not contract for 0.25, as an output of some thousands of kilowatts day and night means adding special plant which, if thrown out suddenly by the financial failure of the process, would have to be idle till the demands of the station caught up with it, and even then the dynamos would have to be altered. In buying energy from a modern power station, without contributing to the capital, the price would probably be about 0.3 per kilowatt hour.

If the process owns its own steam generating plant, it would be safe to allow for part of the cost being covered by 5 per cent debentures.

The idea of risk profits is this:—Any new process such as this, however satisfactory the results so far, involves risks of failure. There are many chances of difficulties in working on a still larger scale, and chances of new and better processes coming out. The last chance is probably small, because the various problems of smelting copper, lead, zinc, antimony, tin, &c., have all been before the world for many years, and a new process that bids fair to solve all of them in a new way is not likely to be superseded as regards many of them by something else, though it might be as regards one of them. The only real risk is that of all new processes—unforeseen difficulties or expenses. The present process is too far advanced to leave many loopholes, but even then experience of other industries shows that it is not wise to embark in a new scheme unless, after the most searching criticism, the profits on paper are so large as to leave a very wide margin. But to get a fair idea, it is obvious that capital in steam generating plant, or in sites, must not all be counted in as expecting what are here called risk profits.

One kilowatt, at 4 volts per cell, deposits 2.61 tons of zinc a year at a current efficiency of 1. The departure from this current efficiency is minute; but the pressure will probably be reduced considerably with larger vats. Steam plant for a ton of zinc a year thus costs £9 12s., or roughly £10 in capital. To reduce a ton of lead a year by replacement with zinc thus involves a capital of £3, and a ton of copper (cuprous) £5 approximately.

In metallurgy it is usual, and some people find it convenient, to work in "units." For each ton of ore smelted per year, the capital cost of steam plant thus comes out—zinc £0.1 per unit, copper £0.05, lead £0.03 approximately; so that if an ore has 33 units of lead, 20 of zinc, and 10 of copper, and plant is wanted to smelt 100,000 tons a year, the steam plant would cost £350,000.

As to smelting plant, including vats, transformers, agitators, pumps, boiling-down plant, and buildings for all the works other than the generating plant, it may be wise to allow as much as half the steam plant for cost of

* A Paper read before the Faraday Society, June 30, 1903.

process, plant, &c., and another equal sum for working capital.

To begin with, we may work out a rough estimate for treating Bluestone ore in this country, with steam generating plant put up for the purpose. 100,000 tons of ore a year will be taken, the ore containing, as delivered, 22 per cent zinc, 18 per cent lead, iron 4 per cent, manganese 3 per cent, gangue 35 per cent, sulphur 18 per cent, silver 15 ozs. The process would require a capital of roughly £550,000, including the generating plant, with no debentures. This allows nothing for payment of patent rights.

The cost of working would be:—

By 100,000 tons of slimes delivered at £2 10s.	£250,000
" 100,000 tons of ore carried through process, excluding cost of energy	150,000
" Electrical energy	94,200
" Allowance for loss of metals and chlorine, say	15,000
" Cost of realising products	16,000
	£525,200
Profits	341,200

To sales of zinc at £20, lead at £12, silver at 2s., two-thirds of the sulphur at £3, iron oxide at £2, manganese £5 5s. £866,400

This leaves over 60 per cent profit on capital, a profit which would leave a margin even after paying the royalties wished for by the proprietors of the patents.

Suppose, however, energy were bought at no less than 0·4d. per kilowatt hour from a power-supply station. The costs would be increased by £55,800 per annum. But the capital would be reduced to, say, £275,000, making a profit of £285,000 on £275,000, or over 100 per cent.

Another estimate may be taken for different conditions. In this case a water-power works on the waterway from the American lakes to the sea will be considered, dealing with ore from the district above.

Take the ore at zinc 41, lead 15, and silver 2 ozs. This is a real ore, but I have no data as to iron contents. If there is any iron to speak of, there must be little gangue. Also I do not know the value of this ore, but will assume it to be refractory. It will then give a good miner's profit if the ore is taken at £2 a ton delivered on the works. To smelt 100,000 tons a year of such a rich ore as this would need about £500,000, of which half is process plant and half working capital. Electrical energy would be bought at, say, 0·1d. per kilowatt-hour.

100,000 tons Canadian ore smelted in America by water-power:—

By 100,000 tons ore	£200,000
By process expenses	150,000
By electrical energy	73,500
By losses, commission, &c. .. .	30,000
	£453,500
Profits	566,500

To sales of metals £1,020,000

There is thus well over 100 per cent profit on this scheme—of course before paying royalties.

This ore has very little gangue, and in that case it might be worth while to dilute it with poor copper ore, especially if the copper ore contains some other valuable metals, such as zinc, antimony, nickel, or precious metal. Thus if the ore has only 10 per cent of gangue, and a low-grade copper with 3 per cent of copper, 5 per cent of zinc, and 5 per cent of iron, has some 80 per cent of rock; for every ton of the rich ore more than a ton of this poor ore could be run through too. The works would then deal with 100,000 tons of this poor ore with very little extra capital cost or expense, as it is nearly all rock, which is eliminated near the beginning of the process. A little more than £1 10s. a ton for the process should have been allowed for the rich ore, and a poor ore takes a great deal less.

Discussing the different metals in order:—

Antimony.—This metal is very easily extracted from the sulphide, either as brown sulphide or as oxide, preferably as oxide. It can also be got out as regulus by reduction. It does not matter whether the antimony is mixed up with other metals or alone.

Arsenic.—This is almost on all fours with antimony. Like it, its sulphide is very easily converted into chloride. It can be equally easily treated when it is an arsenide of other metals. The chief difficulty of antimony and arsenic arises from the poisonousness of their volatile chlorides. We have done little with arsenic.

Bismuth.—This is a small question. Bismuth would be easy to deal with, as it falls out of solution as oxychloride.

Cobalt.—This comes out as oxide; if nickel is also present, the nickel and cobalt and iron, and perhaps manganese, have to be separated in the wet way. There is nothing special about the problem.

Copper.—This comes out of the transformer as cuprous chloride, which is soluble in the other chlorides. It is deposited as cement copper by zinc, not iron. The process will handle ordinary high-grade copper ores successfully, as any other metal, except iron or manganese, is extracted separately as metal too. The copper is of course free from sulphur, arsenic, iron, antimony, phosphorus, silver, &c. In fact, it is pure. Copper can be equally cheaply extracted from arsenical or antimonial ores; in fact, the ores may have arsenic, antimony, zinc, lead, iron, nickel, gold, silver, cobalt, or anything else, and they are all separately extracted without appreciable extra cost. Poor copper ores will either be concentrated or run in with other richer stuff.

Gold.—When present in copper, lead, or other such ores the gold comes out with the silver. Gold in conjunction with antimony, arsenic, tellurium, and small quantities (per ton) of common metals can be treated as a low-grade ore, and run in with any rich mixed or other sulphide, such as lead, zinc, or even rich copper ore or matte. It is largely a question of carriage, and what ores are near each other and near the works.

Iron.—This metal occurs in zinc and copper ores, and comes out as oxide. This oxide is reckoned at £2 a ton, and is useful as a paint. The value depends on the tint, and this depends on the way it is worked up, a matter we have not yet studied. Good oxide fetches high prices, up to £15 or £20 a ton, but the sale is probably very limited. Assuming the lowest price, £2 is not too much to count upon for paint for preserving iron structures where colour is not an object. The extraction of iron itself is a different question. It would come down as a powder from the fused chloride, and would have to be fused together. It would probably cost something under £10 a ton. It may prove that chemically pure iron, with no trace of phosphorus, sulphur, silicon, or manganese or other impurity, is well worth £10 a ton for making special steels or electrical iron stampings.

Manganese.—This metal, like iron, is a drawback in an ore, as it comes out as dioxide, which is not valuable, though the sale of the manganese from such an ore as Broken Hill slimes is worth considering.

Nickel.—This is much the same as cobalt as far as the process goes. It comes out of the transformer as nickel chloride.

Silver.—The silver comes out separately—that is to say, it is extracted from a lead ore as a rich lead-silver alloy. From copper ores it is precipitated by cement copper from the solution of the chloride. Or it may be thrown down by the Claudet method.

Tin.—Tin ores can be added to the charge of the transformer, or treated alone. There is nothing peculiar about it.

Zinc.—Has been fully discussed. Zinc need not exist in the ore worked.

As it is not possible to give a series of estimates for all the innumerable complex ores, it may be well to give an approximate rule which can be applied to any ore.

Rule for Capital.

For each ton of ore per annum to be treated allow :—

Zinc.. .. .	£0.1	per unit
Copper	£0.05	"
Lead	£0.03	"

and for other metals which are extracted in the metallic state, in proportion, inversely as their equivalents. Metals like iron and manganese or antimony, which are extracted as oxides, do not count. This gives a very rough idea of capital necessary for process plant and working capital. If steam or gas generating plant is to be put down, double this capital.

Rule for Working Costs.

For each ton of ore treated at works allow cost of ore delivered, plus £1 10s. per ton for treatment, including everything but cost of electrical energy, and allow 5 per cent extra on cost of ore to cover all waste.

The cost of energy depends on the metal content and on the cost of generation. Steam may be taken at 0.25, gas at 0.125, and water at 0.1 penny per kilowatt hour.

	Steam power.		Gas power.		Water power.	
	£.	Pence.	£.	Pence.	£.	Pence.
Antimony (if as metal)	0.042	10	0.021	5	0.016	4
Copper	0.0175	4.2	0.009	2.1	0.007	1.7
Iron (as oxide)	—	—	—	—	—	—
Manganese (as oxide)	—	—	—	—	—	—
Lead (de-silverised)	0.0107	2.6	0.0054	1.3	0.0043	1
Nickel	0.038	9	0.019	4.5	0.015	3.6
Silver and gold	Inappreciable.					
Tin	0.038	9	0.019	4.5	0.015	3.6
Zinc	0.0342	8.2	0.017	4.2	0.0136	3.3

The price in pence is added because it gives cents too by doubling.

To find the value of the products, add up all the metals in full, the waste or loss being amply covered by the 5 per cent. The iron and manganese must be omitted, being oxides. Their market is uncertain, and much must not be allowed for them. Some of the sulphur is burnt; it is safe to allow for two-thirds of the sulphur contents of the ore at market price.

The process is thus anything but expensive. To see how this is the case, comparison must be made with other plants. Take a mixed zinc, lead, and copper ore, for example. If we take the corresponding plant on the present system, we have first a concentration plant; next a lead-smelting works with all its adjuncts, including a de-silverisation plant; a zinc works and refinery; and a copper-smelting works with an electrolytic refinery. There can be no comparison as to capital cost. As to working cost, the new process begins by saving the concentration, except for very low-grade ores, or where carriage comes in, and thus saves waste. Though 5 per cent waste has been allowed, there is practically no waste of metals; there is nothing to correspond with the waste of copper, zinc, and lead in smelting. In addition, iron and manganese oxides are got out, and most of the sulphur is obtained as brimstone. In this process a smelting works is independent of ore supply, in the sense that it can work any ores.

If copper ores go up, it can devote its whole energy to zinc and lead, and so on, and the variety of ores is so great that the process cannot enhance the value of the ores to the miners. The supply of ores is thus practically unlimited.

This process is the joint invention of Mr. E. A. Ashcroft and myself. Mr. Ashcroft came on the scene when the process was in the baby or test-tube and patent stage. He took it up from that point, and has developed it, not without the necessary pecuniary food being provided for it, into

a healthy, full-sized process which appears to have the backbone of a giant. Since he joined we have worked together as co-inventors, and he has designed and worked out all the plant and carried out all the works. Mr. Ashcroft has also read a paper on this process before the Institution of Mining and Metallurgy; but the process is so little known that it seemed advisable to offer a paper to the Faraday Society.

I hope no one will object to the introduction of questions of cost. This paper is largely financial. All engineering—electrical, chemical, or otherwise—is purely a question of cost. There may be people who think that Science is not Science unless it is merely useless information. Science really is not Science unless it is, or seems likely to be, of use. Every step of the inception and development of a process like this involves Science, and practically nothing but Science. I have also dwelt rather on the broad questions of the scope of its application than on details, because Mr. Ashcroft's paper goes into details very fully, and should be read with this. I am anxious also that the discussion should not turn on detail difficulties that speakers think we ought to meet, or the impossibility of getting off sulphur by replacement with chlorine, or of electrolyzing zinc chloride on the large scale; because we have transformed and electrolysed on the large scale with perfect success. I am much more anxious to know the Society's opinions on the probable future of such a process as this, and its application to the various ores found in different localities.

My thanks are due to the Metallurgical Trust, Limited, the proprietors of this process, for leave to offer this paper to the Faraday Society.

ON THE LOSS OF SILVER IN ROASTING ARGENTIFEROUS BLENDE.

By G. SANDER.

WHEN argentiferous blendes are roasted in Maletra or Liebig-Eichorn furnaces, a loss of silver occurs, concerning which we have had little or no exact data up to the present. We have therefore carried out the series of experiments given in Table I. By "loss on roasting" we mean the loss of weight sustained by the blende after roasting.

The proportion of the fixed compounds in the blende should thus increase proportionally to that loss. Table II. gives the percentage of the principal elements in the blende.

TABLE I.

Mark.	Loss on roasting. Per cent.	Loss in silver, grms. per ton.		Loss of silver. Per cent.
		Before roasting.	After roasting.	
Blende MV ..	10.50	340	335	11.77
" MP ..	10.05	413	410	10.68
" F ..	11.25	230	227.5	12.15
" C ..	12.70	324.5	330	11.22
" A ..	12.00	375	375	12.00

TABLE II.

Mark.	Per cent.						
	Zinc.	Sulphur.	Lead.	Iron.	Lime.	Magnesia.	BaSO ₄ . Quartz
Blende MV	31.00	22.26	7.50	4.25	1.60	0.65	24.50 2.75
" MP	41.80	27.40	4.00	3.00	1.40	0.80	10.55 10.20
" F	43.93	24.95	7.35	5.20	0.10	0.15	— 15.46
" C	47.50	33.26	2.15	13.60	—	1.20	— 1.14
" A	42.60	29.07	8.75	7.50	0.12	1.10	— 10.00

The percentages of silver were determined in the following manner:—20 grms. of the oxidised mineral and 20 grms. of lead were fused together in an iron crucible, and the silver estimated in the lead separated. As by this method there may be losses of silver if the ore contains

sulphur, we added to the roasted ore the amount of sulphur lost by roasting, so as to obtain comparative results. This addition of sulphur varied from 4 to 6 grms, according to the composition of the blende. It was found, however, that this addition of sulphur was useless. The differences obtained by making the estimation with or without the addition of sulphur never exceeded 5 grms. of silver per ton of ore.

An examination of the last column of Table I. shows that the losses of silver are about the same, though the roastings were done at two different works. It must not be imagined, however, that the loss of silver is always 10 or 12 per cent of the amount present, for it depends above all on the temperature at which the furnace is maintained. This loss must be attributed especially to the volatilisation of the metallic silver formed, and it should be greater as the temperature of the furnace is higher.

The raw blende, as a rule, contains its silver in the form of sulphide; this latter is transformed into sulphate during the roasting, and, at the end of the operation, when the temperature has risen to over 900°, into metallic silver, sulphuric and sulphurous anhydrides, and oxygen.

A portion of the volatilised silver should be recovered in the dust chamber. In fact, dust has been recovered from these chambers containing 500 grms. of silver per ton, although the original blende did not contain even 250 grms. per ton.

These dusts contain also 25 per cent of lead, while the blende contained 9 per cent, showing that a portion of the lead, still undetermined, is also volatilised.

I will mention here that many points in connection with the roasting of blendes require examination from the chemical point of view, especially the manner in which lead, lime, and magnesia behave in the presence of silicic acid.

The proportion of sulphur does not only affect the zinc, but also the compounds of lead and silver in the residues.—*Zeitschrift für Angewandte Chemie*, 1902, p. 353.

THE MAZZA SEPARATOR FOR GASES.*

By Capt. VITTORIO CALZAVARA,

Technical Manager of the Società Civile Veneta per l'Industria del Gas ed Elettricità, Editor of the Monthly Technical Review *Il Gas*.

(Concluded from p. 69).

THERE ought thus to be no difficulty in admitting that centrifugal force also, which by the will of man can attain a most important intensity, acting always by its nature on a plane, can succeed in separating gaseous molecules with divers masses.

Having premised as much, we shall now mention those applications which appear to us as most advantageous and surest in connection with the gas industry, which is the one of most interest to those who have attended this Congress.

The density of the principal components of lighting-gas varying greatly, as is known, and such variations happening within rather broad limits, we understand easily how the separation of the same by means of the Separator presented no difficulties; this separation was obtained in numerous experiments made at the works of the Società Italiana del Gas, in Turin, and as the indexes of density most approximate among each other, of the principal components of lighting-gas (depurated from hydro-sulphuric acid, ammonia, and cyanogen) can easily be grouped in two principal large divisions, we shall see how their grouping occurs, when the mixture is subjected to centrifugation in the Separator.

We shall take as a basis a normal analysis of depurated gas, and the density of the air = 1.

	Density.	Volumes.
Benzole, C ₆ H ₆	2.77	0.700
Propylene, C ₃ H ₆	1.498	0.400
Olefiant gas, C ₂ H ₄	0.9674	2.100
Carburetted hydrogen, CH ₄ ..	0.556	37.600
Hydrogen, H	0.06926	46.300
Carbonic oxide, CO	0.9674	11.200
Carbonic acid, CO ₂	1.529	0.800
Nitrogen, N	0.97137	0.900
Total volumes		100.000

We see at once how, by applying centrifugal force to the mixture, the separation will occur between groups having the limits of density farthest, and that we shall therefore have at the central part the grouping of the gases CH₄ and H, the density which is much below the unit (0.556 and 0.06926 respectively), and at the peripheric part the grouping of all the others of which the limits of density vary between 0.9674 and 2.77.

This theoretical presumption has been, in fact, confirmed by the experiments made at the works of the Società Italiana del Gas, in Turin, as their formal declaration proves; it is therefore established that at the centre we shall find a gas almost completely free from heavy carburets which will gather at the periphery.

How can a gas company utilise these mixtures resulting from the separation in an industrial manner? There are numerous ways, and various criteria may be followed, according to the special convenience of each single company.

First of all, the gas collected at the centre may be utilised to great advantage, by carrying out economically the advice given by Lewes, whose great competency is well known, and who recommends us to introduce, by insufflation, hydrogen into the gas-conduits as it issues from the retorts, so as to draw on the heavy carburets which are abundant during the first hours of distillation, and which, as is known, deposit themselves in great quantity to the detriment of the illuminating power of the gas.

At present, on account of the heavy cost of hydrogen produced direct, gas-works adopt the insufflation of air or water-gas, and these diminish, on account of their presence, the increase of illuminating power which would be given by the greater quantity of carburets drawn on by the gas at the issue from the retorts.

It is evident that by employing the hydrogen extracted at a minimum cost from the gas itself with the Separator, the objection on account of the expense disappears, and it will be possible to apply Lewes's excellent advice on a large scale.

If one also consider how extensive to-day, as compared with the past, the use is of gas for heating purposes (kitchens, stoves, incandescent light), the process of separation by means of centrifugal force will bring about remarkable economical results; the increase of heavy carburets which with Lewes's process would be drawn on in the gas to be distributed, corresponds not only to an increase of illuminating power, but also to an increase of heating power; this has been recently shown, and is evident, if we consider that the calorific power of complex lighting-gas is 5500 calories per cubic metre, as against about 2800 calories in hydrogen; and as gas is always sold per cubic metre, we must only take into account the difference in calories with respect to the unit of volume.

There are besides several other separations which the Mazza apparatus has proved capable of effectuating easily, and some of these, according to the requirements and the special conditions of the various works, will certainly be adopted to great advantage.

It is thus possible to depurate lighting-gas completely from hydrogen sulphide and carbonic acid, and this has been already effectually done.

Another important use to which, according to the inventor, the air enriched with oxygen and collected at

* Memoir presented at the Congress of the Deutscher Verein von Gas- und Wasserfachmännern, Zürich, June, 1903.

the periphery of the apparatus might be put, is the rapid and cheap revivification of all matters polluted by the epurators, by passing enriched air through these matters.

Gas companies will, of course, investigate this subject, and have experiments made most carefully; our opinion is, that this depuration could really be effectuated, because, although we are not aware of any such experiments having yet been made, the action of atmospheric hydrogen in such operations has been fully recognised.

As is known to all of us, for reasons over which we have no control, gas companies are now obliged to excoitate all means for utilising the nitrate products of their industry.

First of all, on account of a fact which is the natural consequence of an economical law, the price of gas has been reduced, and the profits formerly realised have been cut down, and great attention has been devoted in view of studying and finding out the best ways and means of utilising sub-products. On the other hand, the increased production, due to the reduction in price, has turned the small percentage of useful nitrogen, found in the immense quantities of coal used, into important quantities, which, as Mr. Boehm, C.E., once justly remarked, represent receipts by no means to be neglected.

Who does not perceive at a glance the immense advantage which the gas industry could derive by using the Mazza apparatus in the preparation of cyanides?

Another application of the Mazza Separator interests the gas trade, as well as all those whose industries need steam; the apparatus in question is specially and, in fact, exclusively suited to feed the steam boiler grates with air enriched with oxygen, by means of centrifugation. We consider it particularly interesting to call attention to this application of the Separator on account of the economical results obtained, as also because the success is beyond all doubt, from the simple fact that the results obtained are no longer experimental, but industrial ones.

The increased yield of fuel almost always reaches 20 per cent, and not seldom does it surpass this figure; the results have been obtained with apparatus which have been working regularly for months, and, as stated, in manufacturing.

The greater yield of the fuel due to the action of the Separator can in no case be attributed to the apparatus considered as a *ventilator*, and this, above all, because feeding with *separated air*, there is constant aspiration under the grate (as is noted daily at Hofmann & Co.'s works, where there is a fluitometre), because the products of combustion are collected at the basis of the chimney, and show a temperature about 20 per cent lower than what they do when ordinary air is employed, and because the saving of fuel is a positive proof of a greater yield, whereas it is well known that the use of ventilators *diminishes* the yield.

It is therefore beyond a doubt that it is the *composition* of the air employed which produces the greater yield of the coal, as it is beyond a doubt that it is the Separator which, by its own action, changes the normal composition of the air in which oxygen, as burning substance, enters in a greater proportion.

We may, finally, mention some other applications of the Separator, the results of which the inventor declares as certain, and which we consider as most probable. Amongst these, the separation and extraction of fire-damp is one of the most remarkable; the danger, now always present, and the terrible results of the combustion of fire-damp in coal mines, would completely disappear by employing the apparatus.

There is also the separation of the products of combustion of carbonic oxide (density 0.9674) from carbonic acid (density 1.529), and the consequent utilisation of the former; experiments have been made most successfully, and anyone can understand the importance of this application in connection with water-gas, and Dowson gas, to be used in gas machines.

We will specially mention only what might be obtained

by carrying out the separation of blast furnace gas, availing ourselves of a very important study on this subject by Signor Emilio Cortese, C.E.

Blast furnace gas is, on an average, composed as follows:—

	Volume.	Weight.	Air density = 1.
Nitrogen	60	58	0.96137
Carbonic oxide .. .	24	24	0.9674
Carbonic acid .. .	12	17	1.5290
Hydrogen	2	0.2	0.06926
Carburetted hydrogen, CH ₄	2	0.8	0.5560
	100.00	100.00	

On coming out of the furnace the gases contain 8 per cent of water vapour, which can be, for the greater part, condensed in the epurators, and between 1 and 5 grms. of dust and powder per cubic metre. The gases, after cooling, are treated by the Separator, and we thus directly eliminate the remaining water vapour, the dust, and, most easily, the carbonic acid, at least for the greater part.

The light mixture would remain composed of nitrogen, carbonic oxide, and carburetted hydrogen; it would thus be considerably enriched by the suppression of at least 17 per cent of its weight in inert gas, and be freed from noxious elements.

It would serve much more efficaciously in motors, because it would not be so poor a gas as Dowson gas, and would be free from dust and powder, the effects of which are disastrous. We may add that, having a gas-generator or a fire-box with a grate at hand, the carbonic acid can be brought in contact with the fuel, and reduced again to carbonic oxide, and thus utilise it profitably. This could, for instance, be useful if one had a Martin furnace with relative gas-generators, near the high furnaces for turning pig-iron into steel.

The possibility of separating gaseous mixtures by means of centrifugal force, and this at a minimum cost, is another application of interest to all great metallurgical works. In fact, besides feeding the fuel with centrifugated and oxygenated air, to increase the smelting temperature, having to provide a certain quantity of CO at the top of the high-blast furnace, so as to obtain certain chemical reactions required for steel working, it would be more convenient to blow under the grate CO₂, derived by centrifugal force from the products of combustion emitted by the high furnace.

The result would be that the CO₂, passing through the strata of incandescent coal, would produce the following reaction, CO₂ + C = 2CO; there would thus be an excess of CO formed without the aid of atmospheric air, and therefore without being accompanied by nitrogen. The centrifugated and oxygenated air would then serve to transform the CO into CO₂, besides profiting by a partial re-utilisation of the C contained in the gaseous products of combustion.

In conclusion, we who have followed most attentively, almost from the beginning, the development and the practical affirmation of Signor Mazza's invention, feel convinced that we may assert that it is destined to have a great success in the industrial world, and, owing to the great variety of its applications, we believe that the adoption of the Separator will give economical results worthy of the greatest consideration.

Magnalium.—We have received samples of a new aluminium alloy "*magnalium*," which will be found useful for many purposes; it has a good silver-white colour, can be forged, and turned easily; the tensile strength is said to be equal to iron, and the electrical conductivity very little inferior to pure aluminium. There is doubtless a large field of usefulness for alloys of this description, and when their value is recognised by manufacturers, much of the apparatus that is now made in brass and gun-metal will be made in the lighter alloy. *Magnalium* can be obtained from the agent, J. Arthur Williams, 92, Hatton Garden, London, E.C.

THE PRESENT POSITION OF THE THEORY
OF ELECTROLYSIS.*

By W. C. DAMPIER WHETHAM, F.R.S.

WHEN, early in the Nineteenth Century, the attention of physicists and chemists was directed to the newly-discovered phenomena of electrolysis, an explanation had immediately to be found for the striking fact that the products of decomposition appeared at the electrodes only, while the body of the solution was unaltered. It was seen that a continual passage of the opposite constituents of the electrolyte in opposite directions through the liquid must be going on, and the chain hypothesis of Grotthus was long accepted as a true picture of the means by which that passage occurred.

About 1830, Faraday, by accurate quantitative measurement, threw new light on the subject, and proved that a definite electric transfer always accompanied a given amount of chemical decomposition. The process of electrolysis now appeared as a kind of convection—a stream of positively electrified cations drifting in one direction, and a stream of negatively electrified anions drifting in the other, under the influence of the electromotive force.

The next step was made in 1853 by Hittorf, who directed attention to the unequal dilution of the solution round the two electrodes, and showed that it could be explained either by the existence of complex ions, by means of which unaltered salt or solvent was dragged to one or other electrode, or by an unequal velocity of movement of the opposite ions. If in any given case we assume or can prove that no complex ions exist, we can calculate the ratio between the velocities of the cation and the anion, for this ratio will be the same as that between the amounts of salt lost by the solution from the neighbourhoods of the anode and the cathode.

In order to determine the absolute velocities with which the two ions move under a given force, it was necessary to discover another relation between those velocities. This was done by Kohlrausch, who pointed out that, on the convective idea of electrolysis, the total electric transfer per second through the solution or the current must be equal to the product of the number of ions, the charge on each of them, and the velocity with which they move relatively to each other—that is, the sum of their opposite absolute velocities. Now, Kohlrausch had already described a satisfactory method of measuring the electric resistance of electrolytes by the use of alternating currents and a telephone, and had shown that, when the reverse electromotive forces at the electrodes were eliminated, the conduction of the current conformed to Ohm's law. The current through the solution would therefore be equal to the product of the conductivity and the potential gradient, and thus a relation was deduced between the molecular conductivity and the sum of the opposite ionic velocities under unit potential gradient—quantities which are known as the ionic mobilities. Combining these results with Hittorf's migration numbers, the absolute values of the ionic mobilities were obtained. Kohlrausch calculated many such mobilities, and showed that, in general, they increased with the dilution of the solution. When several salts containing a common ion, as, for instance, the chlorides of the three metals potassium, sodium, and lithium, were examined, it was found that the values of the mobilities of the common ion chlorine, which differed in the three salts at moderate concentrations, approached each other as the dilution increased, and became identical at a dilution of about 100 litres per gram equivalent of dissolved salt. To such a monovalent ion as chlorine, then, can be assigned a definite specific ionic mobility, which, at great dilution, is independent of the nature of the other ion present.

The first direct experimental confirmation of Kohlrausch's theory was given by Lodge, who measured the velocity with which hydrogen ions travelled along a tube filled with a jelly solution of a salt which contained an indicator,

showing the presence of acid by a change of colour. Further experiments were made by the present writer, who traced the movement of the boundary between two solutions which were themselves of different colours. When the colour difference is due to the cations, the colour boundary travels with the current; when it is due to the anions, it moves against the current. This method has lately been improved and extended by Orme Masson and Steele. The general results confirm Kohlrausch's theory; the observed velocities agree with those calculated, and a very close coincidence is found throughout a considerable range of concentration for salts of monovalent ions. For divalent salts, slight discrepancies appear at higher concentrations, indicating the existence of complex ions; in this confirming the results of other lines of research.

The result of the investigations we have described clearly establishes the convective view of electrolysis; opposite streams of ions certainly pass through the solution, with the velocities indicated by Kohlrausch's theory, carrying their electric charges with them. To allow this migration a certain freedom of movement is necessary; how this freedom is secured is another question.

There is evidence to show that the migratory freedom is not produced as an effect of the electric forces, but exists whether or not such forces act. When the reverse polarisation at the electrodes is eliminated by the use of alternating currents or otherwise, it is well known that the conduction of electricity through solutions conforms to Ohm's law. The current is directly proportional to the electromotive force, and any force, however small, will consequently produce a corresponding current. In the body of the liquid, then, there can be no appreciable reverse electromotive forces, and no chemical or other reversible work is done when a current passes, all such work being located at the electrodes. Thus it follows that the current does no work in giving the ions the independence required for their electrolytic functions; the part played by the electromotive force is merely directive, and the only work expended by it goes in moving the ions, which already possess the necessary freedom, against the frictional forces of the viscous medium.

So far our argument shows that under all conditions the ions of a conducting solution possess the freedom which allows their passage through the liquid under the action of an electromotive force, but we have not considered the essential nature of this migratory freedom. Two alternatives seem to present themselves. Either the ions may migrate independently of each other, in accordance with the dissociation hypothesis, or else they may work their way through the solution by taking advantage of the successive formation and decomposition of molecular aggregates, or of collisions between the dissolved molecules, and the consequent possibility of ionic interchanges, in some such manner as is pictured in Grotthus's chain.

Let us assume for the moment the latter hypothesis, and trace the consequences. The solute molecules are scattered throughout a large volume of solvent, and, on this view, the ions work their way along from molecule to molecule of the solute, at the instants of collision between those molecules. Their velocities must therefore depend in some way on the frequency of collision, and this frequency, we learn from the kinetic theory, varies as the square of the concentration of the dissolved molecules. The ionic mobilities then will increase with the concentration, probably approximately as its square, while the conductivity, which, on the convective idea, is proportional to the product of the mobility and the concentration, will vary more or less proportionally to the cube of the concentration. These consequences of the hypothesis are contrary to observation, which shows that in general the ionic mobilities only vary slowly with dilution, usually slightly falling as the concentration increases, while the conductivity of a dilute solution is directly proportional to the first power of the concentration instead of to its cube, and increases more slowly than the concentration as the solution becomes stronger.

* A Paper read before the Faraday Society, June 30, 1903.

The view which refers the ionic mobilities to molecular interchanges, is thus clearly untenable, and we are driven to examine further the hypothesis of ionic dissociation. Here may be emphasised the point that the dissociation indicated by the electrical properties of solutions is merely a dissociation of the ions from each other, and does not require the supposition that they are free from all chemical combination; forces would certainly exist between the ions and the solvent, and there seems no reason to assume that chemical union between them cannot occur. Molecular complexes with an ion for a nucleus may exist, definite compounds may be formed, or some kind of double decomposition result in the production of new molecules, in which an ion retains its electric charge. About these various possibilities the electrical evidence has nothing to say, an effective migratory independence from each other is all that the ions need to produce the observed phenomena.

The dissociation theory, reached by the arguments outlined above, is supported, and was indeed originally suggested, by other relations. The possibility of assigning specific ionic mobilities, which are independent of the other ion present, is strong evidence for mutual ionic independence. The additive nature of the properties of electrolytes—their colours, for example—though perhaps too much stress has sometimes been laid on it, still tells the same tale. These and other similar arguments are familiar to all readers of text-books on the subject, and need not here be considered in detail. Evidence less well known is given by the power possessed by electrolytes of coagulating certain colloidal solutions, such as those of the sulphides of arsenic and antimony. It has been found by Schulze, by Linder and Picton, and by Hardy (Schulze, *Journ. Prakt. Chem.*, 1882, xxv., 431; Linder and Picton, *Journ. Chem. Soc. Trans.*, 1895, lxvii., 63; Hardy, *Journ. Physiol.*), that this coagulative power stands in a remarkable relation to the valency of the reacting electrolyte, the relative effects for salts with monovalent, divalent, and trivalent ions being represented by the ratios 1 : 30 or 40 : 1000 or 1600. Such results are explicable on the view that the modification of conditions which results in coagulation is produced by the action on a colloid particle of a certain minimum electric charge (Whetham, *Phil. Mag.*, 1899, 5, xlviii, 474; also Hardy and Whetham, *Journ. Physiol.*, 1899, xxiv., 288). An equal charge is brought up by the conjunction of two triads, three diads, or six monads, and, by the principles of the kinetic theory; this relation leads to the values for the ratios of the coagulative powers of 1 : x : x^2 . Putting x equal to 30 or 40, we get, within the limits of experimental error, an exact concordance with the observed results. This explanation has lately been supported by an experiment of Hardy, who finds that the less penetrating rays from radium, which consist of positively charged particles, comparable in size with the hydrogen atom, are likewise able to induce coagulation in solutions of proteid (*Journ. Physiol.*, xxix.; Appendix, p. xxix.).

Thus, taken together, the electrical properties of aqueous solutions yield an overwhelming amount of evidence in favour of the migratory independence from each other of the ions of the dissolved substances. The same conclusion has been reached by an entirely different method of research.

The theory of osmotics rests on a thermodynamic basis, from which we may approach it in two ways. We may accept the pressure-solubility relations of gases, and deduce the results by a thermodynamic cycle in a cylinder with semi-permeable diaphragms, in the original manner of van 't Hoff (*Phil. Mag.*, 1888, 5, xxvi., 88), which has been followed by Lord Rayleigh (*Nature*, 1897, lv., 253), or we may with Willard Gibbs, von Helmholtz, and Larmor (Gibbs, *Trans. Connect. Acad.*, 1875, iii., 138; von Helmholtz, *Abhandlungen*, 1883, iii., 101; Larmor, *Proc. Cambridge Philos. Soc.*, 1897, ix., 240; *Phil. Trans. A.*, 1897, cxc., 205), treat the subject from the fundamental ideas of the molecular theory. By the latter method we must regard the solute as distributed throughout the

solvent as a number of discrete particles, each of which may effect, either by way of chemical combination or physical influence, a certain minute volume of the solvent lying round it. The nature of this influence is unknown but, whatever it may be, as soon as the solution becomes so dilute that, except for an inappreciable fraction of the time, these spheres of influence do not in general intersect each other, any further addition of solvent will only increase the separation of these spheres of action; it cannot change the internal condition of one of them, that is, it cannot affect the interaction between the solute particles and their surrounding solvent. The change of available energy produced by the entry of solvent, must then simply be that due to the dilution of the solute particles, and cannot depend on any interaction between solute and solvent. Now the osmotic pressure which a solution will exert against a solvent is measured by the rate of change of the available energy of the system when solvent is allowed to enter the solution reversibly through a semi-permeable membrane. The osmotic pressure then must, from what we have said above, be independent of the nature of the solvent, and will, therefore, have the same value if no solvent be present. Thus, in cases where this is possible, that is for volatile solutes, it follows that the osmotic pressure must be equal to the gaseous pressure corresponding to the same concentration. In this way we establish, theoretically, the gaseous laws for the osmotic pressure of volatile solutes, and, since volatility is probably only a matter of degree, it seems reasonable to extend this result to non-volatile bodies. Whether this extension be regarded as theoretically valid or not, there is abundant experimental evidence that it is practically justified, since the osmotic pressure of such substances as cane-sugar is well known to have the gaseous value.

(To be continued).

REPORT ON THE SEPARATION OF NITROGENOUS BODIES.*

By L. L. VAN SLYKE.

THE referee decided to confine his work this year to the proteolytic products of milk and cheese in the hope of preparing methods of estimation which could be later subjected to critical examination at the hands of different analysts. The work covered by this report has been largely done in the laboratory of the New York Agricultural Experiment Station, at Geneva, by Mr. E. B. Hart. This report is more accurately entitled "Methods for the Estimation of the Proteolytic Compounds contained in Cheese and Milk."

When milk-casein and its salts, or paracasein in cheese and its salts, are acted upon by dilute acids or alkalis under certain conditions, or by enzymes, or by micro-organisms, the proteid bodies are split up, forming a variety of complex cleavage products. The extent and intensity of such proteolytic changes are measured by the proportions and kinds of the different compounds resulting from the decomposition. In the ripening process that takes place in cheese, we have an instance of extensive proteolysis in the case of the nitrogen compounds of the fresh cheese, due probably to the combined action of dilute acid, enzymes, and micro-organisms. In our study of the causes that produce cheese-ripening and of the conditions that influence the process, we were, at the start, brought face to face with the difficulty involved in the lack of satisfactory methods for making quantitative separations and determinations of the products of cleavage formed. While we have well-elaborated methods for estimating the amount of casein and albumin in fresh milk, these are of little aid in studying the products of their decomposition. Little attention has been given to the development of methods that are applicable to the products occurring in this field. Serious difficulties are in-

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

volved in such a study. First, we know at present only in an extremely meagre and vague way the chemical constitution of milk-casein and its allied compounds. As regards the constitution of the various compounds formed by the proteolysis of casein, we are largely in the dark, except in the case of some of the simpler ones. In the second place, this field is difficult to study, because the quantities of individual compounds that we have to work with are usually very small. Under these conditions, methods of quantitative separation must, at best, be regarded as largely empirical, and more or less tentative. Instead of estimating individual compounds, about which our chemical knowledge is complete, we are compelled, in a large degree, to estimate groups of compounds, the individual members of which we know, for the most part, incompletely or not at all.

From the peptic digestion of casein, Chittenden has separated the proto- and deuto-caseoses ("Studies in Physiol. Chem.," Yale Univ., 1884-85, ii., 156), and from a tryptic digestion, a deuto-caseose and a peptone ("Studies in Physiol. Chem.," Yale Univ., 1887-88, iii., 66), Alexander (*Zeit. f. Physiol. Chem.*, 1898, xxv., 411) has separated hetero-caseose from a peptic digestion of casein, but only in small quantities. Many investigators have observed paranuclein or pseudonuclein, the insoluble residue remaining from the peptic digestion of casein or paracasein. Emil Fischer and P. A. Lavene (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 170) have obtained pyrrolidin- α -carbonic acid from a tryptic digestion of casein.

By hydrolysis of casein with hydrochloric acid, Cohn (*Ber.*, 1896, xlix., 1785) obtained 1-parahydroxyphenyl- α -amidopropionic acid (tyrosin), 1- α -amido-isobutylic acid (leucin), amidosuccinic (aspartic) acid, α -amidoglutamic (glutamic) acid, a pyridine derivative, and ammonia; by the same means, Emil Fischer (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 151) has recently isolated, among the mono-amido acids, in addition to products previously obtained by others, amidovaleric acid, phenyl- α -amidopropionic acid (phenylalanine), pyrrolidin- α -carbonic acid, and probably amido-acetic acid (glycocol).

Among the crystallisable end-products which have been found in ripening cheese are the following:—Tyrosin, leucin, histidin, α - ϵ -diamidocaproic acid (lysin), tetramethylenediamine (putrescin), pentamethylenediamine (cadaverin), lysatin, guanidine probably, and ammonia. Most of these products have been recently reported by Winterstein and Thöny (*Zeit. f. Physiol. Chem.*, 1902, xxxvi., 28) as being found in Emmenthaler cheese. Excepting cadaverin and guanidine, they had also been previously found, though not reported, in American cheddar cheese in this laboratory. It is very probable that other amido compounds will be found, sooner or later, among the products formed by the tryptic, if not the peptic, digestion of milk-casein and of cheddar cheese.

In cheese we find, earlier or later, during the ripening process, a series of compounds and groups of compounds, which, so far as we know at present, appear in something like the following order of succession:—(1) Paracasein, (2) unsaturated paracasein lactate, (3) paranuclein (pseudonuclein), (4) caseoses (albumoses), (5) peptones, (6) amido-acid compounds, and (7) ammonia. After the early stages of ripening we have present at the same time all these different compounds and groups.

We shall consider methods for the separation and estimation of the proteolytic products found, first in cheese, and second in milk, following the general order indicated above. It may be well to say at the outset that in dealing with the separation of nitrogenous bodies so complex in composition as those mentioned above, and occurring in very variable quantities, we can hope at present in the study of milk and cheese problems only to approximate accurate quantitative results. While we have in the Nencki method a very accurate means of estimating ammonia, the methods used in separating peptones from amido compounds can not be relied upon to give us more than approximate results.

I. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF CHEESE.

The description and discussion of the methods used for the separation and estimation of the nitrogen compounds of cheese will be presented in the following order:—

1. Obtaining sample.
2. Determination of total nitrogen in cheese.
3. Extraction of water-soluble products.
4. Determination of total water-soluble nitrogen.
5. Determination of nitrogen in the form of paranuclein.
6. Determination of nitrogen in the form of proteids coagulable by heat in neutral solution.
7. Determination of nitrogen in the form of caseoses (albumoses).
8. Determination of nitrogen in the form of amido-acid compounds.
9. Determination of nitrogen in the form of peptones.
10. Determination of nitrogen in the form of ammonia.
11. Determination of nitrogen in the form of unsaturated paracasein lactate.

1. Obtaining Sample of Cheese.

A sample of cheese is obtained for analysis by means of a cheese-trier, which enables one to secure a round plug of cheese about half an inch in diameter and four to six inches long. Four or five plugs are drawn, one within a short distance of the centre of the cheese, one about an inch from the outer circumference, and the others at points equidistant between the two previous ones taken. Samples thus taken represent practically all different conditions existing in the cheese. After each plug of cheese is removed, about an inch of the end having the rind is cut off, and the rest is placed in a well-stoppered, large-mouthed sample bottle. The end with the rind is dipped once or twice in melted paraffin, and then carefully replaced in the cheese, being pushed in a little below the surface. After all the plugs have been taken and the ends properly replaced in the cheese, some of the melted paraffin is poured over the surface to fill up and surround the depressions made by replacing the ends of the plugs. This treatment generally ensures the exclusion of moulds, and prevents abnormal loss of moisture in the portions of cheese near the holes left by the removal of the cheese-plugs. This is a matter of much importance, when one intends to keep the same cheese for one or two years for systematic examination.

When all the plugs of cheese needed have been taken, the analysis should not be long delayed. The cheese in the bottle is cut into small pieces with a spatula, and stirred within the bottle, in order to mix the whole into as homogeneous a mass as possible.

2. Determination of Total Nitrogen in Cheese.

We weigh out 1 or 2 grms. of the cheese, prepared as described above, for the determination of total nitrogen, and treat it according to the Kjeldahl-Gunning method, modified as follows:—When the solution has become partially digested, we add a piece of copper sulphate about as large as an ordinary pea. Unless this is done, it will take a long time to convert the organic nitrogen completely into ammonia.

3. Extraction of Water-soluble Products.

In a porcelain mortar, we thoroughly mix 25 grms. of our cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. This mixture is transferred to a 450 c.c. Erlenmeyer flask, to which we add about 100 c.c. of distilled water at a temperature of 50° C. The flask is then placed on a water-bath or in some place where it can be kept at a temperature of 50° to 55° C., and is allowed to stand for half-an-hour, being vigorously shaken from time to time. The liquid portion is then decanted through a filter of absorbent cotton into a 500 c.c. flask. The residue is again treated with 100 c.c. of water,

heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 c.c., exclusive of the fat, which usually is present at the top of the liquid.

The cotton filter mentioned is made of two layers of absorbent cotton prepared as follows:—In a glass funnel we place some absorbent cotton to the depth of about 1 inch; moisten this with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this we pour our portions of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 c.c. of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles, and can be returned to the flask for extraction with salt solution.

The method of making a water extract of cheese, as described above, insures the complete removal of all water-soluble nitrogen compounds present in the cheese without danger of coagulating any soluble proteids. The use of water at room temperatures is not, in our experience, equally effective in making a complete extraction of the water-soluble products. Under some conditions, as in the early stages of ripening cheese at low temperatures, small amounts of a body are extracted by water which is precipitated by heat in neutral solution. We are unable to say at present whether this body consists of acid salts of paracasein or of hetero-caseose, which are practically insoluble in water, or whether it is some other compound. The temperature of 50° C. also has the advantage of arresting further peptic or tryptic action during the extraction. The use of acids in extracting cheese is to be avoided, since a small amount of acid will not only precipitate the soluble nuclein, but may form salts with paracasein, which are somewhat soluble in a slightly acid solution; the amount of dissolved paracasein salts under such circumstances depends on the amount of acid used and the time of extraction.

4. Determination of Total Water-soluble Nitrogen.

For the determination of the amount of total water-soluble nitrogen, we take 50 c.c. of the water extract, prepared above, equivalent to 2.5 grms. of cheese, and treat it according to the Kjeldahl method for determining nitrogen.

5. Determination of Nitrogen in the Form of Paranuclein (Pseudonuclein).

To 100 c.c. of the water extract, equivalent to 5 grms. of cheese, we add 5 c.c. of a 1 per cent solution of hydrochloric acid, and warm the mixture on the water-bath at 50° to 55° C. until complete separation takes place, as shown by a clear supernatant liquid. The precipitate is filtered, washed with water, and then, with the filter-paper, treated by the Kjeldahl method to determine the amount of nitrogen. The nitrogen equals nitrogen present in the form of paranuclein (pseudonuclein).

In our early work 2 or 3 c.c. of a saturated alum solution were used for this determination, for the reason that in the separation of casein in milk we had used this reagent successfully; but at the time the nature of the body we were precipitating from our water solution of cheese was not known. Later, when we had studied it and learned its character, it was found, on comparing precipitations, by use of alum and by hydrochloric acid, that alum gave high results, undoubtedly precipitating some caseoses. In 27 comparative trials with water extracts of different cheeses, we found in the alum precipitate nitrogen varying from 0.2 to 0.337 per cent of the cheese, and averaging 0.269 per cent, while the nitrogen in the hydrochloric acid precipitate varied from 0.046 to 0.145 per cent of the cheese, and averaged 0.085 per cent. The nitrogen precipitated by alum in these 27 cases was from 2.1 to 5.5 times as much as that precipitated by hydrochloric acid, the average of all being 3.2. Since hydrochloric acid is known to

precipitate paranuclein completely, we are justified in assuming that the alum precipitates other compounds, and this is confirmed by other work, showing that when alum is used as the first precipitant we get smaller quantities of caseoses in the filtrate than we do when we use hydrochloric acid as the precipitant of paranuclein. Alum appears to resemble zinc sulphate as a precipitant of proteids.

Paranuclein (pseudonuclein) results from the breaking down of casein or paracasein, and is always found in the water extracts of ripening cheese, whether salted or unsalted. It may, perhaps, be regarded more accurately as a residue, and probably should not be counted as one of the products to be used in measuring the extent of cheese ripening. This is undoubtedly the same body as Chittenden's dyspeptone ("Studies in Physiol. Chem.," Yale University, 1887-88, iii., 66), which he found as an insoluble residue in a pepsin-hydrochloric-acid digestion of casein.

6. Determination of Nitrogen in the Form of Proteids Coagulable by Heat in Neutral Solution.

The filtrate from the preceding determination (5) is made neutral with dilute caustic potash, using phenolphthalein as an indicator. It is then heated at the temperature of boiling water, until any coagulum that forms settles completely, leaving a clear supernatant liquid. The precipitate is washed with water, and its nitrogen determined by the Kjeldahl method. In our experience, such a precipitate rarely occurs, except in the case of cheese ripened near freezing-point. The nature of this body we have not yet investigated.

7. Determination of Nitrogen in the Form of Caseoses (Albumoses).

The filtrate from the preceding determination (6) is treated with 1 c.c. of 50 per cent sulphuric acid, saturated with chemically pure zinc sulphate, and then warmed to about 70° C. until the caseoses separate completely and settle. The mixture is allowed to cool, and is then filtered. If filtered hot, there will occur a further separation of caseoses in the filtrate on cooling. The precipitate is washed with a saturated solution of zinc sulphate made slightly acid with sulphuric acid. The nitrogen in the precipitate is determined by the Kjeldahl method.

For the determination of caseoses, the use of ammonium sulphate was exclusively employed until Bömer (*Zeit. Analyt. Chem.*, 1895, v., 562) proposed the use of zinc sulphate, which possesses a distinct advantage in enabling one to determine nitrogen directly in the precipitate or filtrate. This method has been employed, in the estimation of caseoses, also by the Wisconsin Agricultural Experiment Station. In the present state of our knowledge of this class of compounds, zinc sulphate must be regarded as the most available reagent for their quantitative separation.

8. Determination of Nitrogen in the Form of Amido-acid Compounds.

The amido-acid compounds are determined in the filtrate from the precipitation of peptones (9). For the removal of peptones three reagents have been commonly used:—(1) Tannin and sodium chloride, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. After the removal of peptones the filtrate contains amido-acid and ammonia compounds. After determining the amount of total nitrogen in this filtrate, and then the amount of nitrogen present in the form of ammonia (as obtained in 10, see *prox.*), we subtract the amount of ammonia nitrogen from the combined amount of amido-acid and ammonia nitrogen, and thus obtain the amount of amido-acid nitrogen. In the following section (9) we describe the methods involved in removing peptones by the different reagents and the efficiency of each reagent.

(To be continued).

NOTICES OF BOOKS

Twenty-seventh Annual Report of His Majesty's Inspectors of Explosives; being their Annual Report for the Year 1902. London: Darling and Son, Ltd., and Eyre and Spottiswoode. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1903. Pp. 234.

THE only modification of the law made during the past year with regard to explosives, has been the order of the Secretary of State relative to the packing of chlorate mixtures.

Owing to the conclusion of the war in South Africa, the manufacture of explosives for the War Department has fallen away to comparatively small dimensions, but this has been counterbalanced by an increase in the demand for explosives for more useful purposes, so that the end of the war has been of advantage to the trade in general.

As the result of their visits of inspection to the various factories and magazines throughout the kingdom, the inspectors find no reason to complain that there is any falling off in their condition and management. A large portion of their time has been devoted as usual to visiting stores and registered premises throughout the kingdom; they regret to say, however, that though in some places these stores and registered premises are well looked after, in general the administration of the Explosives Act by local authorities leaves much to be desired. Their experience in this respect has led them to the conclusion that in the case of so highly technical an Act, decentralisation is undesirable.

The number of deaths (13) from accidents by fire or explosions, though not high, is above the average for the decade; it will, however, compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or licence is 150; of this total, four factories are under notice of temporary disuse. Four factories have become extinct during the year, and there have been five applications for licenses for new factories, and there were four outstanding from 1901, making nine in all. There have been sixteen new explosives added to the authorised list and four removed from it, with five alterations in definition.

It will be seen from Dr. Dupré's report, Table I., that out of 406 samples examined by him, 36 were rejected; 3 samples of blasting gelatin were rejected out of a total of 43; 12 samples out of 28 of carbonite; none out of 14 of dynamite; none out of 51 of gelatin dynamite; 1 out of 113 of gelignite; and 1 out of 5 of saxonite.

During the year there were four prosecutions for illegal manufacture.

The amount of foreign blasting explosives containing nitroglycerin imported during 1902 is greater than in 1901, the figures being 1,839,277 lbs. against 1,473,950 lbs. The importations of blasting explosives not containing nitroglycerin shows a considerable falling off; the figures were for 1902, 12,000 lbs., and for 1901, 142,900 lbs.

In connection with their visits of inspection the Inspectors found it necessary to institute proceedings in two cases, being the same number as in 1901. Particulars of these cases are given in Appendix T (a). In addition to the above cases, proceedings have been taken by the local authorities in 6 cases on behalf of, or on information supplied by, the Inspectors.

It is to be regretted that the working of the Act by the local authorities is so unsatisfactory. Out of 103 places inspected during the year, the majority being towns, no less than 43 have been classed as "Indifferent" to "Very Bad"; and in these there may be said to be real danger to person and property from the neglect of those precautions in regard to the keeping of explosives which the Act enjoins. Specially noteworthy among these are the City of London, the City of Glasgow, the City of Manchester, and the Rugby division. It is satisfactory to read, however, that in the first three of the above cases, the local authorities have taken steps to put matters on a more satisfactory

basis. In most instances the cause of this unsatisfactory state of things is simply apathy on the part of the local authority and its officer; there are, however, other causes which militate against the efficient administration of the Act. One of these is the frequent changing of the officers appointed by the local authorities, and the consequent difficulty these officers have in acquiring a thorough knowledge of their duties.

Chemical and Pharmaceutical Industries. ("Les Industries Chimiques et Pharmaceutiques"). By ALBIN HALLER, Membre de l'Institut. In Two Volumes. With 108 Figures. Paris: Gauthier-Villars. 1903. Pp. 405 and 445.

THESE two volumes form the report of the Chemical Jury of the International Exhibition of 1900, and deal with the whole subject in a most thorough and comprehensive manner.

As with other exhibits, those of chemical and pharmaceutical products were more particularly exhibits of manufactured articles, but while recognising the inherent difficulties attending a rigorous classification of materials so various as those forming the subject of this work, the author has formed them into chapters, among the principal of which we may mention those on "Artificial Colouring Materials and Extracts of Dye-woods"; "Products of Dry Distillation—Petroleum"; "Natural and Synthetic Perfumes"; "Mineral Colours, Lakes, and Varnishes"; "Soaps"; "Artificial Silks"; and "Colonial Products."

Each chapter deals in a general manner with the special industry which is described therein, its development, and the modifications it may have undergone during the last ten years. Then follows a list of the principal exhibitors in that particular class, with details of their exhibits. Finally, the most important discoveries or improvements in each particular line are summarised.

There is a short index at the end of each volume.

Subject-list of Works on Architecture and Building Construction, in the Library of the Patent Office. Bibliographical Series, No. 9. London: Darling and Son, Ltd. 1903. Pp. 164.

LIKE those that have preceded it, this subject-list consists of two parts:—(a) A general alphabet of subject headings, with entries in chronological order of the works arranged under these headings; (b) a key, or summary of these headings shown in class order.

The present list comprises 1344 works (71 serials, 1273 text-books, &c.), representing some 3173 volumes. The catalogue entries relating to these works number 1739, and are distributed under 217 headings and sub-headings.

Analysis, Detection, and Commercial Value of the Rare Metals. By Dr. J. OHLY, Ph.D. Industrial Printing and Publishing Company, Denver, Colorado, U.S.A.

THIS small treatise will be found of considerable value to those engaged in work upon the rare metals. It contains in small compass much useful information difficult to collect from other sources. Each of the rare metals is treated under six heads:—History, Chemistry, Mineralogy, Detection, Qualitative and Quantitative Estimation. The historical accounts are particularly interesting, and have been introduced to stimulate research by showing the manner in which the difficulties encountered in the discovery and isolation of the various elements have been overcome. In dealing with the mineralogical data, the occurrence of rare minerals in America has been developed more fully than in the case of foreign localities. A good deal of attention has been given to the now very important uranium ores (the source of radium), both in the body of the work and in the appendix; this latter contains some useful matter not strictly connected with rare metals; for instance, the estimation of sulphur in coal, the electric furnace, and the analysis of crude petroleum.

Unfortunately there is no index, and one has to be content with a very meagre "table of contents," but for all that the work will be found of value to assayers, chemists, and prospectors, for whose special benefit it has been compiled.

CORRESPONDENCE.

THE SCINTILLATIONS OF RADIUM.

To the Editor of the Chemical News.

SIR,—Having removed the pointer with the speck of radium nitrate from my Spinthariscopes with the object of testing some minerals for radio-activity, I looked into the apparatus first to ascertain that all was dark, but was surprised at seeing, not only several large motionless stars (which I suppose may be due to radium nitrate deposited when the pointer dropped on to the screen whilst removing it), but a considerable number of bright scintillations—brighter and larger than those in the "luminous sea" seen when the pointer is present. If not troubling you too much, will you kindly say whether you have observed this, and what explanation can be given?—I am, &c.,

C. S. STANFORD WEBSTER.

[The phenomena have been already described. See CHEMICAL NEWS for April 3, 1903.—Ed. C. N.]

CHEMICAL NOTICES FROM FOREIGN SOURCES

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 2, July 13, 1903.

Combination of Ferric Sulphate with Sulphuric Acid.—A. Recoura.—Ferric sulphate combines very easily with sulphuric acid, giving rise to an acid containing one molecule of ferric sulphate and one molecule of sulphuric acid, which the author calls ferrisulphuric acid. This acid is a light white powder which is very soluble in water, giving a pale yellow solution. Analysis shows it to have the formula $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$.

Action of Carbon Monoxide on Iron and its Oxides.—Georges Charpy.—The action of carbon monoxide on iron and its oxides is important, on account of its relation to metallurgical reactions. When sesquioxide of iron is heated in a continuous current of carbon monoxide, the complete reduction of the oxide takes place, and metallic iron—more or less carburated—is left. The reaction takes place at all temperatures between 200° and 1200°, but is naturally more rapid at the higher temperatures.

So-called Colloidal Silver.—M. Hanriot.—The so-called colloidal silvers which the author examines have definite chemical composition and properties. It is proved that the albumenoid matter in collargol and the silver in silvencargol do not constitute impurities, but form an integral portion of the molecule, not only because it is apparently impossible to separate the constituents without destroying the colloidal silver, but also because these bodies have lost their reactions and habitual solubilities. All colloidal silvers when heated in a vacuum evolve carbon dioxide and hydrogen, and have a greater reducing power than that of the silver they contain.

Action of Hypophosphorous Acid on Diethylketone and Acetophenone.—C. Marie.—When hypophosphorous acid acts on diethylketone and acetophenone, the acids $\text{PO}_2\text{H}_3(\text{C}_2\text{H}_5)\text{CO}(\text{C}_2\text{H}_5)$ and $\text{PO}_2\text{H}_3(\text{CH}_3)\text{CO}(\text{C}_6\text{H}_5)$ are produced. The existence of these two acids, when compared to those of the acids prepared by means of PO_2H_3 and the other ketones, whether symmetric or non-symmetric, fatty, or aromatic, show that the reaction by which they are formed is a general one, and is the same as the oxida-

tion reaction which gives the corresponding oxyphosphinic acids.

Phenylpropargylidene Chloride, $\text{C}_6\text{H}_5\text{—C}\equiv\text{C—CHCl}_2$.—Ernest Charon and Edgar Dugoujon.—With the exception of the isomeric transformations of hydrocarbons, the preparation of phenylpropargylidene chloride affords the first example of the action of the triple liaison on the hydrocarbon group, and on the chlorated substitutions in this group. The authors believe that, in the case of chlorated substitution, the triple liaison is less accentuated than that of the double liaison.

Preparation of Secondary Amides.—J. Tarbouriech.—By making the acid chlorides of a number of carbon atoms differing from those of the primary amides, the author obtains mixed or disymmetric amides—a series of which no member, up to the present time, has been prepared. He successfully prepares the following members of the series:—Normal dibutyramide, di-isobutyramide, di-isovaleramide, and normal divaleramide.

Action of Ammonium Persulphate on Metallic Oxides.—A. Seyewetz and P. Trawitz.—When ammonium persulphate acts on metallic oxides reactions take place, which differ considerably from those taking place with hydrogen peroxide. With protoxides a displacement of the ammonia takes place with a probable formation of the corresponding persulphate, or the production of sesquioxides or peroxides. This latter reaction is particularly interesting in the preparation of precipitated lead peroxide. With the sesquioxides or peroxides, it is possible either to produce oxidation of a portion of the ammonia by evolving nitrogen at the same time as the sulphate corresponding to the oxide is produced, or the formation of the oxide with evolution of the oxygen from a portion of the persulphate; or, finally, complete peroxidations, as those obtained with chromium and manganese hydrates.

Action of Bromine on Pinene in presence of Water.—P. Genvresse and P. Faivre.—The action of bromine on pinene has been the object of many researches, and many contradictory results have been arrived at. The authors re-investigate this reaction by another method. They operate in presence of water, care being taken that the temperature is kept low. The oil obtained is retained by the water vapour. A colourless liquid is first produced lighter than water, which consists chiefly of unaltered pinene; after this a yellow oil heavier than water is obtained from which cymene can be extracted, and, finally, a liquid which crystallises. There remains in the apparatus a viscous brown residue. The crystals so obtained melt at 167°–168° after crystallisation from acetic ether. They form a saturated compound, and analysis shows them to have the formula $\text{C}_{10}\text{H}_{16}\text{Br}_2$ (pinene dibromide). M. Wallach obtained these by another method. The formation of this substance is of great importance because it shows the divalence of pinene.

MISCELLANEOUS.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held July 30th the diploma of "Associate of the City and Guilds Institute" was awarded to the following matriculated third year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—

Civil and Mechanical Engineering.—J. D. Griffin, R. C. Munro (Siemens Medal), H. H. Baxter, H. F. Bayley, W. E. G. Bender, G. W. M. Borns, C. E. Capito, J. R. Fox, E. A. Gatehouse, C. J. Gutmann, V. B. Harley-Mason, W. H. Hingston, E. W. Lace, E. Latham, E. de Lautour, R. E. Lehurax, F. E. Maynard, J. E. M. McGregor, H. W. Nicholson, T. C. Ormiston-Chant, D. A. S. Porteous, L. F. Rampal, M. K. Rice-Oxley, F. Salberg, E. A. Salt, C. F. Satow, A. E. Scoones, J. H.

Segrave, C. G. Smith, V. C. Smith, C. E. Thomson, T. W. Wallace.

Electrical Engineering.—A. A. Gomme (Siemens Medal and Premium), J. M. de Artola, W. A. Burton, W. G. H. Cam, F. Creedy, R. S. Dahl, A. G. Ellis, E. P. Elwin, S. F. W. Finnis, A. L. Glegg, C. E. Greenslade, G. R. Griffin, P. H. Harding, M. S. Kennedy, A. H. Knight, T. F. Lee, L. Lehuraux, H. M. Lyons, F. Neuhaus, C. Petersen, H. S. Plymen, R. H. Turrall, L. D. Wainwright.

Chemistry.—E. F. Armstrong, R. J. Caldwell, J. V. J. Hayman, C. D. McCourt, F. J. Salmon.

In addition to the above, Certificates have been awarded to 26 matriculated third year students who have completed a full course of instruction at the Central Technical College, and to 55 students who have completed a full course of instruction at the Technical College, Finsbury.

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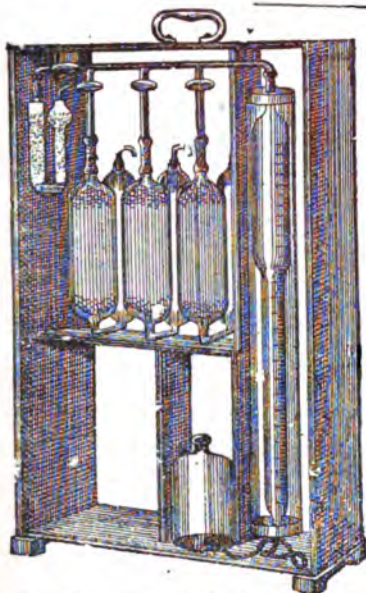
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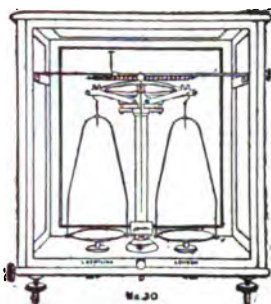
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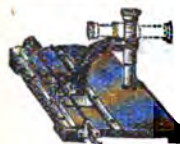
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2282.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKŁODOWSKA CURIE.

INTRODUCTION.

THE object of the present work is the publication of researches which I have been carrying on for more than four years on radio-active bodies. I began these researches by a study of the phosphorescence of uranium, discovered by M. Becquerel. The results to which I was led by this work promised to afford so interesting a field that M. Curie put aside the work on which he was engaged, and joined me, our object being the extraction of new radio-active substances and the further study of their properties.

Since the commencement of our research we thought it well to hand over specimens of the substances, discovered and prepared by ourselves, to certain physicists, in the first place to M. Becquerel, to whom is due the discovery of the uranium rays. In this way we ourselves facilitated the research by others besides ourselves on the new radio-active bodies. At the termination of our first publications, M. Giesel, in Germany, also began to prepare these substances, and passed on specimens of them to several German scientists. Finally, these substances were placed on sale in France and Germany, and the subject growing in importance gave rise to a scientific movement, such that numerous memoirs have appeared, and are constantly appearing on radio-active bodies, principally abroad. The results of the various French and foreign researches are necessarily confused, as is the case with all new subjects in course of investigation, the aspect of the question becoming modified from day to day.

From the chemical point of view, however, one point is definitely established:—i.e., the existence of a new element, strongly radio-active, viz., radium. The preparation of the pure chloride of radium and the determination of the atomic weight of radium form the chief part of my own work. Whilst this work adds to the elements actually known with certainty a new element with very curious properties, a new method of chemical research is at the same time established and justified. This method, based on the consideration of radio-activity as an atomic property of matter, is just that which enabled M. Curie and myself to discover the existence of radium.

If, from the chemical point of view, the question that we undertook primarily may be looked upon as solved, the study of the physical properties of the radio-active bodies is in full evolution. Certain important points have been established, but a large number of the conclusions are still of a provisional character. This is not surprising when we consider the complexity of the phenomena due to radio-activity, and the differences existing between the various radio-active substances. The researches of physicists on these substances constantly meet and overlap. Whilst endeavouring to keep strictly to the limits of this work and to publish my individual research only, I have been obliged at the same time to mention results of other researches, the knowledge of which is indispensable.

I desired, moreover, to make this work an inclusive survey of the actual position of the question.

I indicate at the end the particular questions with which I am specially concerned, and those which I investigated in conjunction with M. Curie.

I carried on the work in the laboratories of the School of Physics and Chemistry in Paris with the permission of Schützenberger, late Director of the School, and M. Lauth, actual Director. I take this opportunity of expressing my gratitude for the kind hospitality received in this school.

* Thesis presented to the Faculté des Sciences de Paris.

HISTORICAL.

The discovery of the phenomena of radio-activity is connected with researches followed, since the discovery of the Röntgen rays, upon the photographic effects of phosphorescent and fluorescent substances.

The first tubes for producing Röntgen rays were without the metallic anti-cathode. The source of the Röntgen rays was the glass surface impinged upon by the cathode rays; this surface was at the same time actively fluorescent. The question then was whether the emission of Röntgen rays necessarily accompanied the production of fluorescence, whatever might be the cause of the latter. This idea was first enunciated by M. Henri Poincaré.

Shortly afterwards, M. Henry announced that he had obtained photographic impressions through black paper by means of phosphorescent zinc sulphide. M. Niewenglowski obtained the same phenomenon with calcium sulphide exposed to the light. Finally, M. Troost obtained strong photographic impressions with zinc sulphide artificially phosphorescent acting across black paper and thick cardboard.

The experiences just cited have not been reproduced, in spite of numerous attempts to this end. It cannot therefore be considered as proved that zinc sulphide and calcium sulphide are capable of emitting, under the action of light, invisible rays which traverse black paper and act on photographic plates.

M. Becquerel has made similar experiments on the salts of uranium, some of which are fluorescent.

He obtained photographic impressions through black paper with the double sulphate of uranium and potassium.

M. Becquerel at first believed that this salt, which is fluorescent, behaved like the sulphides of zinc and calcium in the experiments of MM. Henry, Niewenglowski, and Troost. But the conclusion of his experiments showed that the phenomenon observed was in no way related to the fluorescence. It is not necessary that the salt should be fluorescent; further, uranium and all its compounds, fluorescent or not, act in the same manner, and metallic uranium is the most active. M. Becquerel finally found that by placing uranium compounds in complete darkness, they continue acting on photographic plates through black paper for years. M. Becquerel allows that uranium and its compounds emit peculiar rays—uranium rays. He proved that these rays can penetrate thin metallic screens, and that they discharge electrified bodies. He also made experiments from which he concluded that uranium rays undergo reflection, refraction, and polarisation.

The work of other physicists (Elster and Geitel, Lord Kelvin, Schmidt, Rutherford, Beattie, and Smoluchowski) confirms and extends the results of the researches of M. Becquerel, with the exception of those relating to the reflection, refraction, and polarisation of uranium rays, which in this respect behave like Röntgen rays, as has been recognised first by Mr. Rutherford and then by M. Becquerel himself.

CHAPTER I.

RADIO-ACTIVITY OF URANIUM AND THORIUM.

RADIO-ACTIVE MINERALS.

Becquerel Rays.—The uranium rays discovered by M. Becquerel act upon photographic plates screened from the light; they can penetrate all solid, liquid, and gaseous substances, provided that the thickness is sufficiently reduced; in passing through a gas, they cause it to become a feeble conductor of electricity.

These properties of the uranium compounds are not due to any known cause. The radiation seems to be spontaneous; it loses nothing in intensity, even on keeping the compounds in complete darkness for several years; hence there is no question of the phosphorescence being specially produced by light.

The spontaneity and persistence of the uranium radiation appear as a quite unique physical phenomenon. M. Becquerel kept a piece of uranium for several years in the dark, and he has affirmed that at the end of this time the

action upon a photographic plate had not sensibly altered. MM. Elster and Geitel made a similar experiment, and also found the action to remain constant.

I measured the intensity of radiation of uranium by the effect of this radiation on the conductivity of air. The method of measurement will be explained later. I also obtained figures which prove the persistence of radiation within the limits of accuracy of the experiments.

For these measurements a metallic plate was used covered with a layer of powdered uranium; this plate was not otherwise kept in the dark; this precaution, according to the experimenters already quoted, being of no importance. The number of measurements taken with this plate is very great, and they actually extend over a period of five years.

Some researches were conducted to discover whether other substances were capable of acting similarly to the uranium compounds. M. Schmidt was the first to publish that thorium and its compounds possess exactly the same property. A similar research, made contemporaneously, gave me the same result. I published this not knowing at the time of Schmidt's publication.

We shall say that uranium, thorium, and their compounds emit *Becquerel rays*. I have called *radio-active* those substances which generate emissions of this nature. This name has since been adopted generally.

In their photographic and electric effects, the Becquerel rays approximate to the Röntgen rays. They also, like the latter, possess the faculty of penetrating all matter. But their capacity for penetration is very different; the rays of uranium and of thorium are arrested by some millimetres of solid matter, and cannot traverse in air a distance greater than a few centimetres; this at least is the case for the greater part of the radiation.

The researches of different physicists, and primarily of Mr. Rutherford, have shown that the Becquerel rays undergo neither regular reflection, nor refraction, nor polarisation.

The feeble penetrating power of uranium and thorium rays would point to their similarity to the secondary rays produced by the Röntgen rays, and which have been investigated by M. Sagnac, rather than to the Röntgen rays themselves.

For the rest, the Becquerel rays might be classified as cathode rays propagated in the air. It is now known that these different analogies are all legitimate.

(To be continued).

THE PRESENT POSITION OF THE THEORY OF ELECTROLYSIS.*

By W. C. DAMPIER WHETHAM, F.R.S.

(Concluded from p. 79).

THE direct measurement of osmotic pressure is a matter of considerable difficulty, but there exists a theoretical connection between that pressure and certain other properties of the solution, such as the lowering of its vapour pressure and the depression of its freezing-point below the corresponding values for the pure solvent. Observations on the boiling- or freezing-points of solutions, then, enable the osmotic pressures to be calculated. As is well known, direct osmotic determinations, as well as the results of experiments on these correlated properties, yield abnormally great values in the cases of aqueous solutions of electrolytes. It was van 't Hoff's investigation of this phenomenon that originally suggested the idea of ionic dissociation to Planck and Arrhenius. Since the thermodynamic theory shows that the osmotic pressure of dilute systems depends only on the number and not on the nature of the dissolved particles or on the nature of the solvent, when the osmotic properties have abnormally great values for dilute solutions,

it must follow that the number of dissolved particles is greater than that calculated from the chemical formula weight; that is, that dissociation must have occurred. It does not necessarily follow that the dissociation is that with which we have to deal when examining the electrical properties; whether it is or is not, is a matter for further inquiry. Complicated molecules, dissolved in non-aqueous solvents at any rate, seem sometimes to undergo dissociation into parts which are not electrical ions, for Kahlenberg has lately found that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, and yet are non-conductors of electricity (*Journ. of Phys. Chem.*, 1901, v., 344; 1902, vi., 48). On the other hand, it is difficult to see how more than one kind of dissociation is possible in such a molecule as potassium chloride, which we have already seen is dissociated into electric ions when dissolved in water.

In cases where the dissociation indicated by the osmotic pressure is found to be electrical in its nature, two separate relations have usually been held as necessary consequences of the dissociation theory. How far such suppositions are justified we will proceed to discuss.

The equivalent conductivity of a solution of a simple salt such as potassium chloride increases with dilution, and finally becomes constant. There seems reason to believe that the salt is then completely dissociated into its ions, which, in this case, are shown by the chemical and electrical properties to be two in number. If the osmotic phenomena are examined at dilutions corresponding to complete electrolytic dissociation, we ought to find indications here also that the molecule of potassium chloride behaves as though it were separated into two parts—the osmotic pressure and the freezing-point depression should possess double their normal values.

The only satisfactory measurements at the extreme dilutions necessary are those described by Mr. E. H. Griffiths to the British Association in 1901. The freezing-points of a solution of cane-sugar, as measured by the most accurate methods of platinum thermometry, were such that the molecular depression maintained a value of 1.858 from concentrations of 0.0005 to 0.02 normal. Taking 79.4 as the best value for the latent heat of fusion of water, the result, calculated thermodynamically from the gaseous value of the osmotic pressure, is 1.857. A solution of potassium chloride gave results which increased as the concentration diminished, finally reaching a value of 3.720 at a concentration of 0.0003 gram. equivalents per litre. Twice 1.857 is 3.714, agreeing, within very small limits of experimental error, with the observed result.

For no other electrolytes are such accurate cryoscopic data yet available. The observations of Loomis, which are put forward by Raoult in his recent work ("Cryoscopie," Paris, 1901) as in themselves trustworthy and in accordance with the best of the other known results, were carried only to concentration of 0.01 normal. At this concentration were found values for various binary electrolytes which approach the theoretical result within a few per cent. Substances which, like barium chloride or sulphuric acid, are shown by their electrical behaviour to produce three ions, gave a molecular depression of freezing-point some 10 per cent below the figure for complete dissociation, while salts with two divalent ions, such as magnesium sulphate, fail to reach 3.714 by about 30 per cent. In all these cases the discrepancies are in the direction suggested by the electrical conductivities, which, especially for the last class of salts, indicate that the dissociation is very far from complete at the concentration used in the cryoscopic experiments.

On the whole, then, the evidence is clearly in favour of the relation we are examining, in those cases which have been adequately examined at sufficiently great dilutions.

It has usually been considered that the dissociation theory required a further relation between the electrical and the osmotic measurements. At higher concentrations the equivalent conductivity diminishes, and this is held to denote incomplete ionisation. The actual value of the

* A Paper read before the Faraday Society, June 30, 1903.

equivalent conductivity, divided by its value at extreme dilution, is commonly taken as measuring the fractional coefficient of ionisation, which can obviously be also calculated from osmotic data on the assumption that each dissolved particle still causes the effect it would produce at infinite dilution. Many discrepancies between the values given by these two lines of research have been discovered, and it is necessary to examine how far the theory really suggests any coincidence.

The electrical value of the coefficient of dissociation assumes that no complex ions are present, and that the ionic viscosity of the solution is the same as that which the solvent offers to the passage of the ions at infinite dilution. It is probable that small errors are introduced by these assumptions, but on the other side much larger ones are possible. The deduction by the principles of thermodynamics of the gaseous value for the osmotic pressure is only valid for dilute systems—systems, that is to say, between the parts of which there are no appreciable forces. It is true for a gas at atmospheric pressure; it is true for a non-electrolyte at moderate dilution; but, as Dr. Larmor pointed out to the writer, we must not assume that inter-ionic forces will vanish at corresponding concentration.

In the light of our present knowledge, it is natural to represent a non-dissociated molecule as an electrical bipolar system. The forces between the widely separated molecules of the dissolved substance will be analogous to the translational forces between two small magnets at a distance from each other large compared with the length of either of them. Such forces vary inversely as the fourth power of the distance, and therefore become insensible as soon as that distance exceeds a very small value. Inter-molecular effects, then, will vanish for the solute at moderate dilutions, and the osmotic properties conform to the gaseous laws.

On the other hand, representing an electrolyte in solution as chiefly composed of dissociated ions, we see at once that the forces between those ions are those between isolated particles, charged with opposite kinds of electricity. Such forces vary inversely as the square of the distance, and therefore remain effective at distances whereat the bipolar solute molecules have quite ceased to exert any mutual influence. Inter-ionic forces will thus produce disturbing effects even at very great dilution. The fact that the theoretical value for the freezing-point has been reached in the case of potassium chloride shows that, here at any rate, they vanish at a dilution which, though very great, is still experimentally attainable. It does not follow, however, that they remain insensible as the concentration rises, and the ionisation, determined electrically, ceases to be complete.

Experiments on the comparison of the electrical and the osmotic values of the coefficient of ionisation are now seen to have little use from the point of view of the controversialist seeking arguments for or against the ionic dissociation theory. Such comparisons, however, are of interest, inasmuch as they give data which may enable a more complete theory than we yet possess to take account of the inter-ionic forces which seem to disturb the course of the phenomena except at extreme dilution. Taking as an example solutions of potassium chloride, we may compare the ionisations deduced from electrical measurements by the writer at 0° C. with that indicated by the combined cryoscopic experiments of Griffiths, Raoult, Loomis, and H. C. Jones. The coincidence with theory of Griffith's result shows that the two values agree at extreme dilution, but the cryoscopic curve falls below the electrical one at concentrations of about one-hundredth normal and upwards, reaching a maximum discrepancy (0.84 compared with 0.88) at one-fifth normal, and approaching the higher curve again at greater concentrations. It is possible that the two curves, if prolonged, would cross each other at some considerable concentration. Such chance coincidences probably explain some of the agreements which have been observed between the two lines of research in moderately strong solutions of many salts. More accurate

determinations of freezing-points are needed before such comparisons as these can be taken as a satisfactory basis for theoretical generalisations. Collections of present data have been made by MacGregor (*Phil. Mag.*, 1900, [5], 1., 505), and by Kahlenburg (*Journ. Phys. Chem.*, 1901, v., 399), and further discussion can be found in the writer's book on the "Theory of Solution" (Cambridge, 1902).

The modern theory of the galvanic cell, based on that of the concentration cell, involves both electric and thermodynamic considerations. By imagining an isothermal and reversible cycle, carried out by the passage of one electric unit through the cell, and the reversal of all the chemical and concentration changes by other means, the electric work, and thus the electromotive force, can be calculated. The original treatment of the subject, due to von Helmholtz, effected the reversal by an imagined process of evaporation and condensation of vapour, but it is now more usual to suppose that the reversal is brought about by producing the necessary changes of concentration by osmotic means. In one or other of these ways, by assuming the gaseous laws, the work done in the second part of the cycle can be calculated, and this is equal to that given out in the first part. It is evident that such a theory, based on the principles of thermodynamics alone, furnishes no evidence, one way or the other, about any definite electrolytic or ionic hypothesis, any more than the thermodynamic theory of osmotic pressure can enable us to decide whether that pressure is produced by chemical affinity or by the bombardment of the membrane by the dissolved molecules. In each case we may either rest content with the correlation of the subject given by thermodynamics, or we may inquire further whether any known picture of the physical nature of the phenomena will give us a satisfactory explanation.

Now one kind of concentration cell may be regarded in a simple manner from the point of view of the dissociation theory. It is a cell in which the total potential difference is that due to the contact of two solutions of the same substance at different concentrations. Let us imagine a strong solution of hydrochloric acid placed in a vertical cylinder, and a volume of water placed above it. The dissociated ions of the acid will both diffuse upward, but the more mobile hydrogen will travel faster than the chlorine. Separation thus occurs, and the water (or dilute solution) is found to take a positive potential relatively to the strong solution. Soon, however, the electrostatic forces between the ions become so great that further separation is impossible, and the opposite ions then diffuse at equal rates. From Kohlrausch's experiments we know the velocity with which any ion moves under the action of a given force, and from a knowledge of the osmotic pressure gradient we can calculate the forces at work. Thus the actual velocities of diffusion can be obtained, and the diffusion constant deduced. It is found to agree in a remarkable manner with the observed diffusivity. Equating the velocities of the two ions we get the condition for no further separation, and obtain an expression for the difference of potential between the two solutions in the form—

$$\frac{RT}{q} \frac{v-u}{v+u} \log \frac{c_2}{c_1},$$

where R is the gas constant for 1 grm.-molecule and of its electric charge, T the absolute temperature, c_1 and c_2 the concentrations, and u and v the coefficients of ionic mobility. Such an expression agrees with that deduced thermodynamically for similar cells, and Nernst, by suitable experimental arrangements, has confirmed it directly. Thus the phenomena of concentration cells may be satisfactorily explained by the hypothesis of independent ionic diffusion.

The chemical reactions of electrolytes, rapid and easily produced, are in marked contrast with those of organic bodies, which are usually attacked slowly and with difficulty. In the original presentment of the dissociation theory Arrhenius pointed out the close numerical con-

nection which exists between the electrical ionisation of aqueous solutions and the coefficients of chemical activity of the dissolved substances.

There is no such definite theoretical deduction of this relation as of that between the conductivity and osmotic effects; the connection of electrical ionisation with chemical activity is a matter of observation, and the conclusion that in the rapid chemical actions characteristic of electrolytes it is the ions which alone are active, rests on the evidence of this connection alone. The numerical relations given by Arrhenius, and the many deductions from this hypothesis which have been verified for aqueous solutions, have led to the idea that a similar explanation of the nature of all rapid chemical action might be given, whatever the solvent and whatever the conditions. There seems, however, no valid theoretical reason which necessitates such an extension, and it is possible that in other solvents, and for gaseous or fused systems, rapid chemical change may be brought about by non-electrical double decomposition. This conclusion is supported by an observation of Kahlenberg on the instantaneous production of a precipitate of copper chloride when hydrochloric acid is passed into a non-conducting solution of copper oleate in benzene (*Journ. Phys. Chem.*, 1902, vi., 1). It is evident that such a result indicates that in the particular solvent used rapid chemical action may occur which is not correlated with appreciable electrolytic ionisation, but it does not in the least affect the electrical and osmotic evidence we have adduced above in favour of the theory of the ionic dissociation of the aqueous solutions of electrolytes. Nevertheless, it serves to caution us against extending the deductions of theory which apply to simple aqueous solutions to cases which have not been subjected to an adequate theoretical and experimental examination.

The recognition of the intimate connection between chemical and electrical phenomena led Ostwald to apply the mass law of chemical action to the effect of dilution on the equilibrium between the undissociated molecules and the ions formed from them in an electrolytic solution. As is well known, this application met with perfect success in the case of weak acids and other slightly conducting solutions, but completely failed to explain the effects of dilution on strong acids and other good conductors. This discrepancy has been considered one of the greatest objections to the dissociation theory. The difficulty, which formerly appeared to the writer a very great one, is probably to be explained by that difference in the law of the variation of the force with the distance which we have already pointed out must exist between solutions containing non-dissociated bipolar molecules and those containing dissociated electrified ions. The inter-molecular forces, varying inversely as the fourth power of the distance, rapidly become insensible with dilution, while those between the ions, depending on the square of the distance, are effective at much higher concentrations. Now the theory of the mass law rests on a thermodynamic basis, and in its deduction the assumption is made that the matter considered is in the dilute state. The work done in forming a small quantity of one of the products of the reaction at a standard pressure, and bringing it to the existing pressure, may then be written in the form $a + RT \log b/c$, where a and b are constants, R the gas constant for 1 grm.-molecule, T the absolute temperature, and C the concentration. Similar expressions give the work done for other reagents or products, reckoned positive when they are formed, and negative when they disappear. When equilibrium is reached, the change of available energy arising from a further slight transformation must vanish, thus the value of $n_1(a_1 + RT \log b_1/c_1) + n_2(a_2 + RT \log b_2/c_2) + \dots$ must be zero, and we see that $C_1^{n_1} C_2^{n_2} \dots$ may be put equal to K , a function of the temperature alone. This result is the mass law, and if we apply it to a solution in which 1 grm.-molecule of electrolyte is dissolved in a volume V , a fraction α being ionised, we obtain the equation

$$\left(\frac{1-\alpha}{V}\right)^{-1} \left(\frac{\alpha}{V}\right)^2 = \frac{\alpha^2}{V(1-\alpha)} = K,$$

Ostwald's dilution law. Its deduction clearly involves the assumption that the gas laws hold good, and that consequently no inter-molecular forces or other similar actions are appreciable. We must not, therefore, look for conformity with the dilution law in solutions where many dissociated ions are present.

Summing up our inquiry as far as we have yet pursued it, we may say that the phenomena of electrolysis, and the osmotic properties of electrolytes, clearly indicate that the conduction of a current through an aqueous solution consists in the convection of charged ions through the liquid, the ions being dissociated from each other while they are electrolytically active.

We must now raise the much wider question, and ask whether this mode of conduction is a universal accompaniment of electrolysis, or whether it is confined to the case of solutions in water. Since the development of the dissociation hypothesis, as applied to liquid electrolytes, a vast increase has occurred in our knowledge of the discharge of electricity through gases. This process has been satisfactorily explained as a convective electrolytic action, the ions being in some cases dissociated molecules, in other cases isolated corpuscles, which may represent the ultimate units of negative electricity, perhaps even the common constituents, aggregates of which make up the different chemical atoms. Such results not only support the idea of a similar dissociation as the cause of the conductivity of solutions, but give a presumption in favour of the general applicability of such theories. When, however, we examine how far such a presumption is justified, further considerations are seen to be involved. Had the phenomena of gaseous conduction been first in the field, we could not, without experimental evidence, have extended a dissociation hypothesis, framed to explain them, to the much more complicated systems which are formed by electrolytic solutions. It is only on the knowledge summarised in the laws of Faraday, Ohm, and Kohlrausch, that the particular phenomena which have led us to the dissociation theory require such an explanation, and at present, it is only for solutions in water, and a few other liquids, that we possess sufficient evidence for those laws, and for the other relations to which we have referred, to enable us to draw valid conclusions. Without definite experimental evidence in each case, we cannot legitimately extend these conclusions, and when, as in fused salts, the conditions are entirely different, we shall presently see that an alternative explanation is possible. Nevertheless, for all solutions which conduct electricity, the presumption in favour of similarity of explanation is very great, and for several solvents, at any rate, experiments show that the general process of conduction is similar to that which we have studied in aqueous solutions.

When we go further, however, and try to trace in non-aqueous media the ionisation of solutes as measured electrically and osmotically, we are met by want of numerical data, largely owing to increased difficulty of experiment. With some solvents, as, for instance, the alcohols, freezing-point work is impossible, and in no case do measurements of osmotic properties appear to have been made at dilutions great enough to enable us to fairly treat the systems as thermodynamically dilute. On the electrical side more data are available, but the examples of acetic acid and ammonia show that, even in water solutions, complete ionisation cannot always be experimentally attained, and, without definite evidence, it is not safe to conclude that in another solvent it can ever be reached. We have already seen that only when the dissociation is complete can a just comparison be made between the numbers of ions given by a molecule as determined electrically and as determined osmotically. Thus it is necessary to push the dilution so far, that the equivalent conductivity reaches a definite limiting value before making such comparisons. Limiting values have been obtained for salts of the alkali metals dissolved in methyl and ethyl alcohols (Fitzpatrick, *Phil. Mag.*, 1887, xxiv., 378; Völlmer, *Wied. Ann.*, 1894, 328; Zelinsky and

Krapiwin, *Zeit. Phys. Chem.*, 1896, xxi., 35), in acetone (Carrara, *Gazz. Chim. Ital.*, 1897, xxvii., i., 207; Laszozynski, *Zeit. Elektrochem.*, 1895, II., 55; Dutoit and Aston, *Comptes Rendus*, 1897, cxxv., 240), and in pyridine (Laszozynski and Gorski, *Zeit. Elektrochem.*, 1897, IV., 200), but in all these cases no osmotic data have been determined at dilutions great enough to secure complete ionisation, or to justify the gaseous laws as applied to the osmotic phenomena. Experiments at higher concentrations are of little value, for not only do the disturbing causes already noted in the case of aqueous solutions act here also, but it is known that one of them, the influence of complex ions, is much more common and much more important. (Comparisons of electric and osmotic data for non-aqueous solutions have been collected by Lincoln, *Journ. Phys. Chem.*, 1899, iii., 457). It is probable too that association of the non-ionised solute molecules may occur, Kahlenberg, for instance, having discovered cases in which the boiling- or freezing-points of conducting solutions indicate that the number of such molecules is less than the chemical formula would lead one to expect (*Journ. Phys. Chem.*, 1901, v., 342). It is evident that the existence of such association does not in the least prevent the conduction of the current by the movement of charged ions dissociated from each other. Such observations as those referred to have been brought forward as evidence against the whole basis of the theory of ionic dissociation, but the relations on which they bear are, as we have seen, merely consequences of the theory under ideal conditions of very restricted nature, and are not, as seems to be so commonly supposed, the very foundation on which the theory rests.

Faraday found that many fused salts were electrolytes, with conductivities of the same order as those of aqueous solutions, and since his time it has been confirmed that, in such cases, the electro-chemical equivalents have the usual values (Faraday, "Experimental Researches"; Helfenstein, *Zeit. Anorg. Chem.*, 1900, xxiii., 255). How far are the principles of the dissociation theory applicable to fused electrolytes? No osmotic data are available, and it is difficult to see how such data could be obtained. Let us examine the matter from the electrical side. The products of decomposition appear at the electrodes only, and Faraday's laws hold good; hence the process must be convective, but we have no knowledge of the ionic velocities, and no means of estimating the amount of ionisation. When closely scrutinised, the conditions are seen to be essentially different from those which led to the adoption of the belief in considerable and permanent dissociation for aqueous solutions. We do not know that the conductivity is proportional to the number of ions present, but even if such a relation were established, the consequences deduced from it in the case of solutions would not necessarily follow. The process, as we said, must be convective, and freedom of migration of the ions is necessary, but, unlike a solution, a fused salt consists of a collection of molecules all of the same kind, and the argument from the frequency of collision between dissolved molecules, isolated from each other by comparatively vast spaces of solvent, ceases to be valid. In a fused salt the electrolytic molecules are crowded together, and, even if dissociated ions are present, the interaction of one of them with one of the surrounding electrolytic molecules, which replace the neutral molecules of the solvent of a solution, would make possible an effective interchange, and enable an electric transfer to take place. Thus the frequency of interchange for any one ion would not increase with the ionic concentration as in the case of a solution, and the conductivity might be proportional to the number of ions without permanent ionic dissociation. The conditions are entirely different to those which hold in a solution, where the solvent molecules are of different kind to those of the electrolyte and cannot take a direct part in the electrolytic process. We may now go further, and say that it is possible that conduction in a fused salt may be due to a mere possibility of interchange between the electrified

parts of the molecules, without any permanent and definite dissociation. Some process in the nature of Grotthus's chain may, in this case, secure the migratory freedom necessary for electrolytic conduction. Whether this is so, or whether, as in solutions, the current is carried by ions dissociated from each other, their number being a function of the temperature, remains a question for future investigation.

THE PHENOMENA OF LUMINOSITY AND THEIR POSSIBLE CORRELATION WITH RADIO-ACTIVITY.*

(DYNAMIC ISOMERISM IN RELATION TO LUMINOUS
PHENOMENA).

By HENRY E. ARMSTRONG, F.R.S.,
and
T. MARTIN LOWRY, D.Sc.

THE possibility of regarding *luminous manifestations* generally—including radio-activity—as the outcome of oscillatory changes in molecular structure, has already been pointed out by one of us in a communication made to the Society more than a year ago, in which the kind of change contemplated was exemplified by reference to the case of nitrocamphor (Henry E. Armstrong, "The Conditions Determinative of Chemical Change and of Electrical Conduction in Gases and on the Phenomena of Luminosity," *Roy. Soc. Proc.*, 1902, vol. lxx., p. 99; *CHEMICAL NEWS*, vol. lxxxv., p. 241). As the phenomena of radio-activity are exciting so much interest, it appears desirable to enter somewhat more fully into an explanation of the argument underlying this conception of the origin of luminous appearances.

In the note referred to, it was suggested that *triboluminescent* substances, i.e., substances which become luminous at the moment of crushing, might conceivably, at the same time, manifest radio-activity. Sir William Crookes has recently examined saccharin from this point of view, using freshly prepared crystals which one of us had placed at his disposal. We are much indebted to him for the following account of his observations:—

"The crystals of saccharin, when broken in the dark, gave off flashes of light.

1. A sensitive photographic film was covered with a sheet of aluminium foil 0.04 m.m. thick, and some crystals were broken on the foil. On development no darkening was seen.

2. A similar experiment, in which black paper was used instead of aluminium foil, also gave negative results.

3. Some crystals of saccharin were broken close to the sensitive surface of a photographic film. The flashes of light could be seen through the film. On development some spots were seen on the film, which were caused probably by the light given off.

4. A crystal was broken near the surface of a barium platinocyanide screen. The screen glowed at the moment of the flash from the crystal.

5. A crystal of saccharin was put on a hard surface and a screen of barium platinocyanide was laid face upwards on it. By means of pressure on the screen the crystal beneath was crushed, when a flash of luminosity was seen to cover the screen over the place where the crystal was broken.

6. A screen of hexagonal blende was taken, and Experiments 4 and 5 were repeated with it. The results were negative, except that I fancied there might be a trace of light when the crystal was broken close to the sensitive surface of the screen."

Although it may be argued from Experiment 5 that saccharin is radio-active when crushed, we have been unable hitherto to detect any effect on the electrometer. Through

* A Paper read before the Royal Society, June 18, 1903.

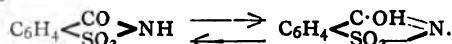
the kindness of Dr. Lapworth we have been able also to examine the menthyl phenylformylacetate recently described by him, a substance capable of existing in isodynamic forms, which is not only intensely tribo-luminescent, but gives out most brilliant flashes of light as it separates from solution, its behaviour in this respect being, if possible, even more striking than that of radium in face of a screen of hexagonal blende to which Sir William Crookes has directed attention. As a small quantity of this substance was crystallising out from petroleum spirit, no fewer than ninety-two flashes were observed in broad daylight in the course of ten minutes. Even this substance, however, has not hitherto given positive results when tested by the electrometer.

Tribo-luminescence.

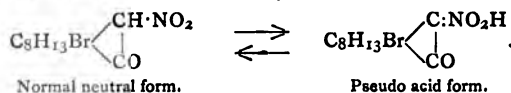
We have now to consider the nature of the change involved in the production of the luminous flash, in order that it may be clear why, in our opinion, if radio-activity were observed in such a case, it would have been as the concomitant to chemical change.

There is distinct evidence that the phenomena of tribo-luminescence may be correlated with the occurrence of the form of isomeric change which attends the passage of a compound into the isodynamic* form of low potential. Tschugaeff (*Ber.*, 1901, vol. xxxiv., p. 1820), who has examined over 500 inorganic and organic compounds, found that about 25 per cent of the latter gave a more or less intense flash when crushed; of these a considerable proportion appear to be such as could exist in isodynamic forms. Only about 5 per cent of the inorganic substances flashed.

To take the case of saccharin, the two conceivable forms are—



Comparable with these are the two isodynamic forms of π - and β -bromonitrocamphor, for example—

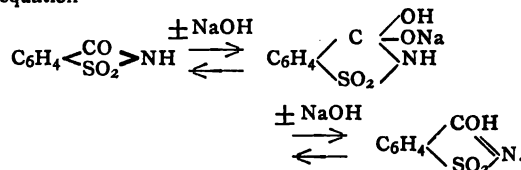


In the solid state both forms of π -bromonitrocamphor are stable: when either form is dissolved in a liquid, isomeric change sets in; sooner or later, it may be only in the course of a few hours or even days, a state of equilibrium is established, about 6 per cent of the material being present in the pseudo-form and 94 per cent in the normal form (compare Lowry, *Trans. Chem. Soc.*, 1898, p. 966; *Proc. Chem. Soc.*, 1903, p. 129). The change, however, does not occur spontaneously, but is undoubtedly dependent on the presence of a catalyst, as equilibrium is established with great rapidity if a trace of alkali be added; acids have only a slight, although definite, accelerating effect. In the case of β -bromonitrocamphor, solutions in benzene of the neutral as well as of the acid form which have been kept during several days without undergoing change, when transferred to another vessel, have rapidly passed to a condition of equilibrium—doubtless because this vessel had been less successfully cleansed than that first used. It can, therefore, scarcely be doubted that the change occurs within a complex system—one which, it is only reasonable to suppose, constitutes an electrolytic circuit. The process is reversed when crystallisation sets in; if the evaporation of the solvent take place sufficiently slowly, the whole of the material is converted into and crystallises out in the less soluble form; if, however, evaporation take place rapidly, the isomeric change may lag behind the crystallisation and both forms may separate. In the case of nitrocamphor, the normal form is the one that separates from the solution; but in the case of π - and β -bromonitrocamphor,

* This term has been introduced by one of us as being more appropriate than the term tautomeric to connote substances which are apparently almost equipotential—as they so closely simulate one another in behaviour under ordinary circumstances—and are easily interconvertible.

although the pseudo-form is the minor constituent in the solution, being much less soluble than the isomeric form, it is one to separate on crystallisation.

The passage of the one form into the other in the case of saccharin, for example, may be pictured as involving the occurrence of changes such as are represented in the equation—

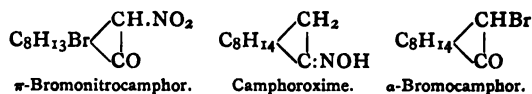


Supposing the stable form of lower potential to crystallise out, the crystals, in almost every case would contain a minute and variable amount of the isodynamic form entangled, as it were, in the mass. In the solid, reversion to the stable form would take place very slowly. Presumably, however, sudden crushing of the crystals would afford opportunity for the change to take place and for the sudden liberation of energy—hence the momentary flash.

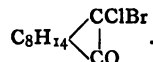
In support of this view we have the fact:—

1. That the phenomenon of tribo-luminescence occurs irregularly in the case of saccharin: being sometimes shown by one crop of crystals and not by another, the highly purified substance—Professor Pope informs us—being inactive.

2. That whereas the phenomenon is observed in the cases of three derivatives of camphor which are obviously capable of existing in isodynamic forms,* viz.,—



it is not seen in the case of camphor derivatives, which, although otherwise similar, cannot exist in isodynamic forms, e.g., α -chloro- α -bromocamphor,—



It is not, at present, necessary to assume that the phenomena are limited to cases of isomeric change; obviously, changes such as those above considered, may be regarded broadly as dissociative or reversible changes; and from this point of view, it is sufficient to regard the phenomena as the outcome of a loss of potential consequent on the passage from an unstable to a stable system. Thus, if Tschugaeff's statement that a salt such as aniline hydrochloride is tribo-luminescent, be confirmed by observation with the highly purified substance, it will be justifiable to assume that when it is crushed, the manifestation of luminosity may be due to the reformation of salt momentarily dissociated by pressure.

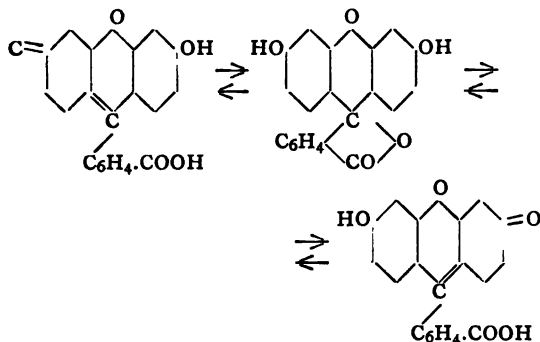
From the point of view here advocated, it would be impossible to construct a condenser from a pure dielectric; and if the dielectric of a charged condenser were suddenly smashed under suitable conditions, it might exhibit the phenomenon of triboluminosity and perhaps radio-activity.

Fluorescence.

It was originally suggested by one of us, in discussing the origin of visible colour, that fluorescence is the "beginning of colour." Subsequently, Dr. J. T. Hewitt, in a paper on the relation between constitution and fluorescence, published early in 1900 (*Proc. Chem. Soc.*, 1900 vol. xvi., p. 3; *Zeit. Phys. Chem.*, 1900, vol. xxxiv., p. 1), took the important step of associating the appearance of

* Nitrocamphor does not flash when crushed; perhaps this is because of its texture. It may be that the effect will be observed at lower temperatures.

fluorescence, not with the mere occurrence of the quinoid type of structure, which one of us has long contended is characteristic of visibly coloured substance, but with the continued development of such a structure—in other words, he has regarded it as the outcome of oscillatory changes in the course of which a non-quinonoid compound undergoes conversion into the isodynamic quinonoid compound,* for example, in the manner represented by the formulæ, which picture the changes undergone by fluorescein:—



According to Hewitt, "all the molecules will be undergoing tautomeric change continuously and frequently, and energy absorbed when the molecules have one configuration will be, to an appreciable extent, emitted when they correspond to the other configuration. It is practically certain that the vibration frequency of fluorescein is different in the two states, and hence every opportunity is offered for energy of a rapid vibration frequency to be largely transformed into energy of greater wave-length."

Hewitt obviously does not regard fluorescence as a "flash phenomenon," but as a form of colour, as it were.

While agreeing with Hewitt that the origin of the effect is to be sought in the occurrence of reversible changes involving the production of dynamic isomerides, we think that fluorescence is to be regarded as something apart from colour, which, more often than not, is superposed upon colour. Colour appears to be dependent upon selective absorption, and scarcely to involve any return of the absorbed energy as light. The character of the colour effect in fluorescence is quite distinctive; it is not only remarkable on account of its intensity, but there is in it an indefinable qualitative difference which seems to separate it from ordinary colour. If regarded as a "flash phenomenon" this difficulty disappears.

Hewitt appears to regard fluorescence as the outcome of mere intramolecular wobble. To us it seems likely that the change is conditioned by a catalyst, and that it occurs within a complex electrolytic circuit. From this point of view, the fluorescence of uranium glass is noteworthy, as showing that changes in molecular structure may go on in a solid viscous medium. It will be desirable to ascertain whether such glass is fluorescent at low temperatures, at which it ceases to be viscous.

Phosphorescence.

The phenomena of phosphorescence need to be considered with reference both to cases in which the manifestation attends oxidative or other kinds of chemical change (the glow of phosphorus, the glow-worm, phosphorescent bacteria), and to those in which it is induced by exposure to light (luminous sulphides). The former might well

almost be regarded as cases of fluorescence, as a continual supply of energy is derived from the continued occurrence of a chemical change involving loss of energy. With regard to the latter, it would seem that it is not a property of pure substances. Thus it is known that the production of sulphides, which can be rendered luminous by exposure to light, is dependent on certain special conditions being fulfilled, that, for example, barium sulphide, which is not sensitive *per se*, becomes highly so when it is associated with a minute proportion of bismuth.*

The phosphorescent medium may be pictured as a complex system, capable of undergoing "electrolytic" deformation under the influence of light of high refrangibility: as the changes thus induced are reversed, the energy stored up during insolation becomes liberated, and the persistence of the effect is but a consequence of the fact that the change takes place under restraint, in a viscous medium.

Dewar's remarkable observations on phosphorescence at low temperatures clearly foreshadow the conclusion that the property is to be correlated with structure. The two most remarkable classes of substances, he states, are the Platinocyanides amongst inorganic compounds, and the Ketonic compounds amongst organic. But these latter are precisely those which are most prone to undergo conversion into isodynamic forms. It is very noteworthy that, according to Dewar, "water when pure is only feebly phosphorescent, but remarkably so when impure."

Radio-activity.

Pursuing the argument a stage further, it appears to us justifiable to regard the activity of radium tentatively, as but an exaggerated form of fluorescence, in which radiations unnoticed by substances generally—capable of penetrating substances generally—become absorbed and rendered obvious. Such an explanation, from the chemist's point of view, is at least as rational as one which assumes that nature has endowed radium alone of all the elements with incurable suicidal monomania, especially as exothermic changes, when once started, have a tendency to occur rapidly, if not explosively.

There seems to be no good reason for assuming that in fluorescent and other ordinary substances, we possess screens capable of arresting rays of every conceivable kind; it may well be that our knowledge of solar radiations is not yet complete; that radium should be more powerful than other substances is not surprising, seeing that of all the elements known to us, it perhaps has the highest atomic weight. It is also worth noting that radium stands in close relation to the elements which afford luminous sulphides.

With regard to "Thorium and Thorium X," the facts, as stated by Rutherford and Soddy, do not seem to be incompatible with the view that these are but isodynamic forms of thorium or their equivalent, their behaviour being very similar to that of the isodynamic forms of nitrocamphor, the rate of decay and recovery of activity proceeding according to a simple logarithmic law, just as does the conversion of one form into the other in the case of nitrocamphor. In any case, it appears desirable to approach the problem from this point of view, and to investigate the phenomena far more thoroughly on the chemical side.

Finally, it may be pointed out that the properties discussed in this note are common to not a few substances. Uranium nitrate is not only radio-active, but triboluminescent, fluorescent, and phosphorescent, at low temperatures; and, as Dewar has shown in a recent Royal Institution lecture, it becomes highly electrified when cooled. Platinocyanides also are triboluminescent, fluorescent, and phosphorescent, at low temperatures.

* In this connection, attention may be called to the following passage which occurs in a note by one of us on fluorescence in quinine salts (*Trans. Chem. Soc.*, 1892, p. 790):—"It is well known that the oxy-salts of quinine are alone fluorescent, salts like the chlorhydrate not being so; it is conceivable that this is due to the inferior stability of the former in solution, and that, owing to the occurrence of dissociation, a condition is engendered favouring the passage by dynamic change from the non-fluorescent centric to the fluorescent ethenoid condition."

* L. E. O. de Visser, *Rec. Trav. Chim.*, 1901, vol. xx., p. 435; 1903, vol. xxii., p. 133. In the case of calcium sulphide, the maximum effect is produced when about 1 atom of bismuth is present to 50,000 of calcium. According to the later paper, bismuth alone does not confer the property, but the presence of a sodium salt in addition makes the mixture sensitive.

That the several manifestations all have their origin in the formation and decay of isodynamic or equivalent systems, is therefore by no means improbable.

Whatever the ultimate value of the considerations advanced in this note, they at least serve to show that much may be learnt by further study of the extent to which luminous phenomena generally are to be correlated with structure and structural changes.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES.*

By L. L. VAN SLYKE.

(Concluded from p. 81).

9. Determination of Nitrogen in the Form of Peptones.

(1) By Tannin and Sodium Chloride.

We place 100 c.c. of our water extract of cheese in a 250 c.c. graduated flask, add 1 gm. of sodium chloride and a solution containing 12 per cent of tannin until one drop added to the clear supernatant liquid gives no further precipitate. We then dilute to the 250 c.c. mark, shake, filter through a dry filter, and determine the amount of nitrogen in 50 c.c. of the filtrate by the Kjeldahl method; this gives us the amount of nitrogen in the form of amido-acid and ammonia compounds. The amount of nitrogen in the form of peptones is determined by difference—that is, by subtracting from the amount of total nitrogen in the water extract the combined sum of the amounts of nitrogen found in 5, 6, 7, 8, and 10.

The combination of tannin and salt has been settled upon by us as the most satisfactory for the separation of casein-derived peptones from amido-acid compounds in milk and cheese analysis, when, as is commonly the case, we have large amounts of amido-acid compounds relative to peptones. We have confirmed Schjerning's (*Zeit. Analyt. Chem.*, 1900, xxxix., 545) results showing that this reagent does not precipitate the monoamido-acid compounds, such as leucine, tyrosine, aspartic acid, glutamic acid, and amido-valeric acid, nor does it precipitate histidine, arginine, lysine, cadaverine, putrescine, lysine, or ammonia. In our work the tannin-salt solution has nearly as great a precipitating power as phosphotungstic acid, precipitating 93.3 per cent of the total nitrogen compounds present in a sample of fresh milk; in a study of ripened cheese it precipitated the uncrystallisable end products, caseoses and peptones, so completely that no further trouble was experienced in separating the crystallisable end products.

It is well to record here the fact that when precipitation of peptones with tannin-salt solution is attempted in a mineral acid solution no precipitation occurs; it is only in neutral solution that more complete precipitation takes place.

The chief objection to the use of tannin-salt solution as a means of separating caseoses and peptones from amido-acid compounds and ammonia is that it is not a complete precipitant of peptones. Hence, when the reagent for this separation is used we commonly leave some peptones to be estimated as amido-acid compounds, the amount of peptones thus being made smaller, and the amount of amido-acid compounds larger than the quantity actually present. Under the discussion of the use of phosphotungstic acid as a reagent for separating these classes of nitrogen compounds are given for comparison some results secured by each of the two reagents.

(2) By Phosphotungstic Acid with Sulphuric Acid.

In a 250 c.c. graduated flask we place 100 c.c. of the water extract of cheese, add 100 c.c. of water, and then 5 c.c. of strong sulphuric acid. To this add phosphotungstic acid of 30 per cent strength until one drop gives no further precipitation in the clear supernatant liquid. Then dilute to the 250 c.c. mark and filter through a dry filter. In 50 c.c. or 100 c.c. of this filtrate we determine the amount of nitrogen

by the Kjeldahl method, and then the amount of peptones is obtained by difference.

Phosphotungstic acid has come into very general use in this country and in Europe as a means of separating peptones from amido-acid compounds in work with cheese and milk. The results of Stutzer (*Zeit. f. Analyt. Chem.*, 1896, xxxv., 1493) and of Bondzynski (*Landw. Jahrbuch der Schweiz*, 1894) agree in showing that phosphotungstic acid is a complete precipitant of casein, caseoses, and peptones, while in their experience it does not precipitate the amido-acid compounds or ammonia. Freudenreich and Jensen in all their work, even of recent date, have used this reagent in the cold as a means of separating peptones from amido-acid compounds. Babcock, Russell, and Vivian, in this country have used it, as well as tannin, designating the different precipitates as "peptones by phosphotungstic acid" and "peptones by tannin."

In the introductory portion of this paper, when mentioning different cleavage products of casein, we included among them the hexon bases, viz., arginine, histidine, and lysine; and, in addition, certain compounds resulting from their cleavage, such as putrescine and cadaverine, and also pyrrolidine- α -carbonic acid, all of which are precipitated by phosphotungstic acid. While all these products have not been separated from ripening cheese, it is probable that they will be sooner or later. We shall soon publish results of work done in this laboratory showing in normal ripening cheese the presence of histidine, lysine, putrescine (derived from arginine) (A. Ellinger, *Ber.*, 1898, xxxi., III., 3183), and Siegfried's lysatin, which is also precipitable by phosphotungstic acid. The quantities of these bases that can be derived from casein are not to be neglected, since, for example, in a hydrochloric acid cleavage 15.4 per cent of the nitrogen of the products splits off into the hexon bases. Bondzynski has used phosphotungstic acid in hot solution with arginine, and finds the precipitate soluble when hot, separating out on cooling; and this statement we can confirm, the solution, however, being complete only on boiling. In the case of lysine, histidine, and putrescine the phosphotungstic acid precipitate fails to redissolve completely at the temperature of the water-bath or on boiling. This behaviour renders worthless the use of phosphotungstic acid as a reagent for the separation of peptones from those amido-acid compounds that are precipitated by it.

We have seen that tannin-salt solution fails to precipitate peptones completely, and that phosphotungstic acid precipitates, in addition to peptones, some amido-acid compounds. When, therefore, we use these two reagents in precipitating solutions that contain both peptones and amido-acid compounds, as in the case of normal ripening cheese, we should expect to find the amount of nitrogen compounds left in the filtrate less with phosphotungstic acid than with tannin. This is found invariably to be the case. Vivian (*"Ann. Rep. Wis. Exp. Sta."*, 1899, xvi., 171) has published some results obtained with nine different cheeses, which illustrate this point. We give his figures in the table following:—

TABLE I.—Comparison of Phosphotungstic Acid and Tannin-salt Solution in Precipitating the Nitrogen Compounds contained in Water Extracts of Cheese.

Sample No.	Precipitating agent used.	
	Phosphotungstic acid.	Tannin-salt solution.
	Per cent.	Per cent.
1.	1.08	1.54
2.	1.00	1.26
3.	0.82	1.12
4.	0.63	0.65
5.	0.67	1.16
6.	1.69	1.87
7.	0.95	1.08
8.	1.10	1.36
9.	1.22	1.42
Average . .	1.02	1.27

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

In connection with the above results nothing was stated in regard to the history of the cheeses used in the work. We have studied the action of phosphotungstic acid and tannin-salt solution in connection with samples of cheese that were under known well-controlled conditions, thus learning something of the general character of the proteolytic changes taking place. Twenty-five grms. of cheese curd were placed in each of several Erlenmeyer flasks, 50 c.c. of water added, and the contents sterilised by heat. We then added 0.5 gm. of concentrated lactic acid, in order to convert the paracasein into unsaturated paracasein lactate ("N.Y. Agr. Expt. Sta.," 1902, ccxiv., 67). To some of the flasks thus prepared sterilised pepsin was added, and to others sterilised rennet extract. For this purpose the enzymes were prepared as follows:—We dissolved 600 m.grms. of Parke Davis and Co.'s aseptic pepsin in 25 c.c. of water, added 0.5 per cent of formalin containing 40 per cent of formaldehyde, and let the solution stand until bacteriological examinations, made by Mr. H. A. Harding, showed the absence of living organisms. The mixture was then diluted to 100 c.c. with water, and to each flask containing cheese we added 10 c.c. of this sterilised pepsin solution. One thousand parts of the mixture in each flask thus contained one part of pepsin.

In preparing the sterilised rennet solution, 5 c.c. of Hansen's rennet extract were diluted to 25 c.c. with water, 0.5 per cent of formalin was added, the completeness of sterilisation proved by bacteriological examinations, diluted to 100 c.c., and 10 c.c. of this preparation added to each flask containing cheese.

The flasks thus prepared were kept at 15.5° C. The analytical results given below were obtained at the end of two and four weeks. In this work, we had only the enzymes of pepsin and of rennet pepsin acting upon our proteid. Under these conditions, especially in the given length of time, we should not expect the formation of any considerable amount of amido-acid compounds precipitable by phosphotungstic acid. The results obtained are given in the following table:—

TABLE II.—Comparison of Phosphotungstic Acid and Tannin-salt Solution in Precipitating the Nitrogen Compounds Formed by Peptic Digestion of Cheese.

Sample No.	Precipitating agent used.	
	Phosphotungstic acid.	Tannin-salt solution.
	Per cent.	Per cent.
1.	0.10	0.45
2.	0.10	0.44
3.	0.150	0.645
4.	0.175	0.685
5.	0.10	0.48
6.	0.08	0.46
7.	0.16	0.73
8.	0.16	0.70
Average . .	0.123	0.574

In every case except one, the amount of nitrogen not precipitated by tannin-salt solution was more than four times the amount obtained by phosphotungstic acid. No ammonia was present in any case. In view of these widely differing results in relation to the amounts of amido-acid compounds found, the questions may be asked:—"Which reagent more nearly represents the amount of amido compounds actually present? Does the tannin-salt reagent fail to precipitate the peptones completely, thus allowing the unprecipitated peptones to be counted among the amido acid compounds? Or does the amount of nitrogen in the filtrate in case of this reagent really represent amido-acid compounds? Does the phosphotungstic acid precipitate some of the amido compounds simultaneously with the peptones, thus cutting out a part of the amido-acid compounds and counting that part among the peptones? Or is there in the cheese only the small amount of end products indicated by the action of the phosphotungstic acid?"

While we did not by individual isolation determine to what extent amido compounds were present, we are justified in believing that such compounds were not yet present in the cheese in any appreciable degree; and, hence, the figures obtained with phosphotungstic acid are much nearer the truth than those obtained by tannin-salt precipitation. The reasons for this belief are as follows:—The amido compounds precipitated by phosphotungstic acid are known to be chiefly the diamido compounds, while the monoamido compounds are precipitated little, if at all. Hence, the compounds found in the filtrate of a phosphotungstic acid precipitation are mainly monoamido compounds. Now let us assume temporarily that the amounts of nitrogen in the tannin-salt filtrate, given in the table above, represent the total amido compounds, free from peptones; then, since the monoamido compounds are represented by the amounts of nitrogen obtained in the phosphotungstic acid filtrate, the difference between the two sets of figures—that is, those obtained by tannin-salt solution and those obtained by phosphotungstic acid—represents the amount of diamido compounds. Taking the average of the results given in the table above, the nitrogen of the total amido compounds is 0.574 per cent of the cheese, while the nitrogen of the monoamido compounds is 0.128 per cent of the cheese, thus leaving the difference as the nitrogen of the diamido compounds, equivalent to 0.446 per cent of the cheese. According to these figures, the monoamido compounds constitute about 22 per cent of the entire amount of amido bodies, while the remainder, 78 per cent, represents largely diamido compounds. In this case, the ratio of monoamido to diamido compounds is as 1 to 3.5. Keeping these data in mind, we will call attention to some work done by Hart (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 347) in studying the cleavage end products formed by the action of hydrochloric acid on casein. He found that the diamido compounds formed less than 20 per cent of the total amido compounds, so that the ratio of monoamido to diamido compounds was as 1 to 0.25 or less; in other words, the monoamido compounds were greatly in excess of the diamido compounds, or just the reverse of what we find to be the case in the results embodied in the table above, based on the assumption that the nitrogen in the tannin-salt filtrate represents the total amido compounds and nothing more. The most obvious and rational explanation of this discrepancy observed in the ratio of monoamido to diamido compounds is that it is wrong to assume that the tannin-salt filtrate contains only amido compounds and not any peptones. Withdrawing that assumption, then, and allowing that the nitrogen in the tannin-salt filtrate represents some peptones as well as the amido compounds, how can we tell in this particular case the true amount of amido compounds in the cheese? Unquestionably the results with phosphotungstic acid more nearly represent the truth in regard to the amido compounds, because under the conditions of the experiment we should expect very small amounts of amido compounds, if any; and in this particular case the amounts are so small as practically to indicate the absence of amido bodies altogether. From this it may be seen that it is possible for the tannin-salt reagent to give results that are decidedly misleading.

(3) By Bromine with Hydrochloric Acid.

To the filtrate from the zinc sulphate precipitate (7) we add 2 or 3 drops of strong hydrochloric acid, and then bromine until the liquid becomes saturated, and there remains after vigorous agitation an undissolved globule of bromine, amounting to 0.5 c.c. to 1 c.c. This is allowed to stand overnight. The precipitate is then filtered and washed with bromine-saturated water. The nitrogen in the precipitate is then determined by the Kjeldahl method, and is called nitrogen in the form of peptones, the filtrate containing the amido-acid compounds and ammonia.

The use of chlorine by Rideal and Stewart (*Analyst*, 1897, xxii., 228) in precipitating proteids suggested to Allen and Searle (*Analyst*, 1897, xxii., 259) the use of

bromine. They reported that bromine quantitatively precipitates the products formed by the peptic digestion of egg albumin, and they developed the method practically as given above. As applied to the separation of peptones from amido-acid compounds in cheese and milk, the method gives varying results, depending upon the age of the cheese or milk used.

In the case of our water extracts made from cheese nine months to a year old, crystalline bodies in noticeable quantities are precipitated by bromine along with peptones, owing probably to the presence of tyrosin, giving the solution a turbid appearance, and rendering filtration difficult. Schjerning (*Zeit. f. Anal. Chem.*, 1900, xxxix., 545) has shown that tyrosin behaves in this manner with bromine water. This precipitate is partly retained on the filter-paper, and is estimated as peptone.

Schjerning has shown also that bromine does not completely precipitate milk proteids and their derived caseoses and peptones. Of the whole proteid he obtained only 76.7 per cent by bromine. In the case of milk we have obtained results varying with the age of the milk. In perfectly fresh milk, when the amount of amido compounds must have been least, we obtained 91.3 per cent of the entire milk proteids by bromine precipitation. In another case of fresh milk we compared the precipitation of proteids by bromine and hydrochloric acid with that by tannin and sodium chloride, and by solution of phosphotungstic acid and sulphuric acid, with the following results:—There was precipitated—

By phosphotungstic and sulphuric acids, 93.8 per cent of the total nitrogen.

By tannin and sodium chloride, 93.3 per cent of the total nitrogen.

By bromine and hydrochloric acid, 91.5 per cent of the total nitrogen.

There is also a possible source of error in connection with the use of bromine in precipitating peptones when the filtrate from the bromine precipitate is used directly for the determination of amido-acid compounds. We have found in the case of water extracts from cheese over one year old that there is an actual loss of nitrogen when bromine is allowed to stand in contact with the water extract. In the case of one cheese two years old, the cheese extract, consisting of caseoses, peptones, and amido-acid compounds, contained nitrogen equivalent to 2.74 per cent of the cheese before adding bromine, while, after standing one hour in contact with bromine in hydrochloric acid solution, there remained only 1.52 per cent of nitrogen; in other words, there had disappeared 44.6 per cent of the nitrogen present before the addition of bromine. In cheese one year old we have found the loss varying from nothing in one case to over 5 per cent in others. To show whether or not this loss came from the action of bromine on the caseoses or peptones we removed the caseoses with zinc sulphate, and in another sample of cheese extract we removed the caseoses and peptones with phosphotungstic acid, and the loss still occurred. By passing a current of air through the above extract in contact with bromine and then through potassium hydroxide and through sulphuric acid, these reagents were found free from nitrogen compounds, indicating that the lost nitrogen disappeared in the form of free nitrogen, and not in the form of ammonia or nitrogen oxides. We cannot regard the method of determining the amount of peptones in cheese extracts by means of bromine as a reliable method, because (1) bromine precipitates small amounts of tyrosin, and perhaps certain other similar compounds; (2) it is not a complete precipitant of caseoses and peptones; and (3) its filtrate cannot be used for the determination of amido-acid compounds, especially in old cheeses, owing to the decomposing effect of bromine upon such compounds setting nitrogen free. In addition, bromine is a most disagreeable reagent to handle.

(4) *Comparative Value of Different Reagents Used in Separating Peptones and Amido-acid Compounds.*

We have now considered in some detail each of the three reagents most commonly used in separating peptones

from amido-acid compounds, viz.:—(1) Tannin-salt solution, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. Tannin-salt solution fails as a perfect reagent for the separation because it does not completely precipitate peptones, which results in making the quantitative results for amido-acid compounds too high, and may indicate the presence of considerable quantities of amido-compounds even when they are practically absent. Phosphotungstic acid, on the other hand, completely precipitates peptones, but also precipitates some of the amido-acid compounds that are present in cheese and milk, and the consequence is that the amount of amido-acid compounds found is too low. Bromine is open to both objections—it fails to precipitate peptones completely, and at the same time does precipitate some of the amido-acid compounds. While these two sources of error might tend to offset each other under certain conditions, we cannot depend upon such a method for reliable quantitative results.

In our judgment, it is desirable, for best results, to use phosphotungstic acid to separate peptones and amido-acid compounds when the amount of amido-acid compounds is relatively small as compared with peptones, or when they consist mostly of monoamido compounds. This condition occurs in the early stages of cheese ripening, and persists longer in cheese cured at low temperatures; it occurs also in milk and cheese acted upon by pepsin enzymes, especially in the presence of chloroform.

Tannin-salt solution can be relied upon to give better results than phosphotungstic acid when amido-acid compounds are present in proportions that are relatively large compared with peptones, or when they consist largely of diamido compounds. The former condition prevails in normal cheese cured under usual conditions, especially after the first two weeks of curing.

10. *Determination of Nitrogen in the Form of Ammonia.*

Distil with magnesium oxide 100 c.c. of the filtrate from the tannin-salt precipitation, passing the distillate into a standardised acid, and titrating in the usual way. In our early work the cheese mass itself, suspended in water, was used for distillation, giving slightly higher results than the method just described. The small increase is generally accounted for as coming from the proteids themselves present in the solution. Theoretically it is true that when such bases are present as putrescin and cadaverin they might distil with the ammonia. In one case, where a large quantity of cheese was subjected directly to distillation with magnesium oxide and the distillate examined for these bases, none was found, the distillate consisting entirely of the ammonia salt. The high boiling-points of cadaverin and putrescin, and the consequent difficulty of distilling them with steam, probably accounts for their absence in the distillate.

In our early work on the determination of ammonia in milk and cheese, we subjected to distillation with magnesium oxide and with barium carbonate many different amido compounds, in order to ascertain if any of these bodies when pure could split off basic nitrogen. While some of the products used in our work are not at all likely to be found in cheese or milk, we include them with the others in the list given below. The method was carried out as follows:—Dissolve 1 grm. of each amido body, or if insoluble, suspend it in 50 c.c. of water, and for distillation use 10 c.c. of this mixture diluted to 150 c.c., adding magnesium oxide or barium carbonate, and using ordinary atmospheric pressure.

Amido bodies used were:—

Acetamide.	Diphenylamine.	Phenylenediamine.
Allantoine (a).	Glutamic acid.	Trimethylamine.
Arginin.	Glyocol.	Tyrosin.
Aspartic acid.	Histidin.	Uric acid.
Creatin.	Leucin.	Xanthin.
Creatinine.	Lysin.	

(a) *Zeit. f. Physiol. Chem.*, 1901, xxxiv., 145.

The result of this work was that nothing was distilled over with either magnesium oxide or barium carbonate in any case except that of trimethylamine, the nitrogen of which was all obtained in the distillate with both reagents.

We have also used the excellent Nencki apparatus, distilling under reduced pressure the filtrate from the tannin-salt precipitation. In comparative trials we have obtained no lower results than when we distil under ordinary atmospheric pressure.

II. Determination of Nitrogen in the Form of Unsaturated Paracasein Lactate.

The residue insoluble in water is treated with several portions of a 5 per cent solution of sodium chloride, the process being carried out as in preparing the water extract (see 3, p. 80). The nitrogen in an aliquot part of the 500 c.c. of this salt extract is determined by the Kjeldahl method.

II. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF MILK AND THEIR PROTEOLYTIC PRODUCTS.

We will briefly describe the methods used for the separation and estimation of the nitrogen compounds of milk and their proteolytic products in the following order:—

1. Determination of total nitrogen in milk.
2. Determination of nitrogen in the form of casein.
3. Determination of nitrogen in the form of albumin and syntonin.
4. Determination of nitrogen in the form of caseoses.
5. Determination of nitrogen in the form of amido-acid compounds.
6. Determination of nitrogen in the form of peptones.
7. Determination of nitrogen in the form of ammonia.

1. Determination of Total Nitrogen in Milk.

Weigh about 5 grms. of milk and determine the nitrogen by the Kjeldahl method.

2. Determination of Casein.

To about 10 grms. of milk add 90 c.c. of water at 104° to 108° F. (40° to 42° C.), and then 1.5 c.c. of 10 per cent acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash, and treat by the Kjeldahl method for estimating nitrogen.

In fresh milk 2 or 3 c.c. of a saturated solution of alum may be used in place of acetic acid, usually with little higher results. But when the milk casein has been proteolysed to any extent, the use of alum is not permissible, since it precipitates caseoses in addition to casein.

The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these two compounds.

3. Determination of Nitrogen in the Form of Albumin and Syntonin.

The filtrate from 2 is neutralised by caustic alkali, using phenolphthalein as indicator, and is then heated at the temperature of boiling water until the precipitate completely separates and settles. The precipitate is then filtered, washed, and treated by the Kjeldahl method.

4. Determination of Nitrogen in the Form of Caseoses.

The filtrate from 3 is heated to 70° C., 1 c.c. of 50 per cent sulphuric acid is added, and then chemically pure zinc sulphate to saturation. Let stand at the temperature indicated until the caseoses completely separate and settle. Then cool the mixture, filter, wash with a saturated solution of zinc sulphate made slightly acid with sulphuric acid, and treat the precipitate by the Kjeldahl method.

5. Determination of Nitrogen in the Form of Amido-acid Compounds.

Treat about 50 grms. of milk with a tannin-salt solution or with phosphotungstic acid according to directions given under 8, p. 81.

6. Determination of Nitrogen in the Form of Peptones.

From the total nitrogen, subtract that found in all forms other than that of peptones, as indicated under 9, p. 92.

7. Determination of Nitrogen in the Form of Ammonia.

See under 10, p. 94.

III. DETERMINATION OF CHLOROFORM.

When chloroform is used as an antiseptic in milk and cheese it is very essential to know approximately the amount present, in order that we may have a proper control of conditions. We have used the following method successfully:—Place 5 grms. of milk or cheese in a pressure-bottle with about 100 c.c. of alcohol and 5 grms. of caustic potash. The bottle is then heated in an autoclave for half-an-hour at 110° C. The resulting chloride is determined by titration, as for chlorine in sodium chloride.

Recommendation.

It is recommended that the methods presented above be adopted as provisional methods under the head of dairy products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxix., No. 5.

All the papers in this number have been noticed already in these columns.

No. 6.

Influence of the Nature of the Cathode on the Quantitative Separation of Metals by Electrolysis.—A. Hollard.—Already inserted in full.

A New Method for the Chlorination of the Aromatic Carbides.—A. Seyewetz and M. Biot.—Already noticed.

Chlorination of the Substituted Aromatic Carbides by Plumbico-ammoniacal Chloride.—A. Seyewetz and P. Trawitz.—Already noticed.

A New Di-iodised Phenol.—P. Brenans.—Already noticed.

A New Orthocyclohexanediol and its Derivatives.—Leon Brunel.—Already noticed.

Some Derivatives of Diphenylamine and of the Tolyphenylamines.—F. Reverdin and P. Crépeux.—As a result of their researches on colouring-matters, the authors have succeeded in preparing some derivatives of diphenylamine and of the tolyphenylamines; with the exception of the *o*- and *p*-tolyl-*o'*-, *p'*-, dinitrophenylamines, these derivatives have not yet been described. Nine new derivatives are described, and their analyses given in this paper.

Benzene-*p*-azobenzoic Aldehyde.—P. Freundler.—Already noticed.

Estimation and Organic Analysis of Very Small Quantities of Glycerin.—Maurice Nicloux.—Already inserted in full.

New Reaction of Cystine.—Ali Riza.—According to Benzinger, cystine gives a white precipitate with mercuric chloride, consisting of a combination of these two bodies. However, mercuric chloride does not give a precipitate

directly with cystine; it is necessary, to obtain it by means of this reagent, to reduce the cystine first with tin or zinc and hydrochloric acid. Under these conditions, it decomposes into two molecules of cystein, which then give the above-mentioned white precipitate with the mercuric chloride. By using acid mercuric sulphate, the author has obtained the white precipitate directly from an acid solution of cystine without having recourse to reduction. To effect this, a small quantity of cystine was dissolved in about 1 c.c. of normal sulphuric acid, and an excess of acid mercuric sulphate added; the precipitate appears in a few seconds.

MISCELLANEOUS.

The Iron and Steel Institute.—The following is the corrected list of the papers to be submitted at the forthcoming meeting of the Iron and Steel Institute at Barrow-in-Furness on September 1st to 4th:—

- "Alloys of Iron and Tungsten." By R. A. Hadfield, Vice-President.
- "The Restoration of Dangerously Crystalline Steel by Heat Treatment." By J. E. Stead, Member of Council, and Arthur W. Richards (Middlesbrough).
- "On Sorbitic Steel Rails." By J. E. Stead, Member of Council, and Arthur W. Richards (Middlesbrough).
- "Influence of Silicon on Iron." By Thomas Baker, M.Sc. (Sheffield).
- "Diffusion of Sulphides through Steel." By Prof. E. D. Campbell (Ann Arbor, Michigan).
- "Heat Treatment of Steel." By William Campbell (New York), Carnegie Research Scholar.
- "Manufacture of Weldless Steel Pipes." By H. Ehrhardt (Düsseldorf).
- "Heat Treatment of Steel Rails high in Manganese." By J. S. Lloyd.
- "Regulation of the Combustion in Coke-oven Practice." By D. A. Louis (London).
- "Coal as Fuel at Barrow-in-Furness." By W. F. Pettigrew (Barrow-in-Furness).
- "On the Diseases of Steel." By C. H. Ridsdale (Middlesbrough).
- "The Probability of Iron Ore lying below the Sands of the Duddon Estuary." By J. L. Shaw (Whitehaven).
- "Overheating and Burning of Steel." By Prof. A. Stansfield, D.Sc.(Lond.), Assoc.R.S.M. (Montreal), Carnegie Research Scholar.

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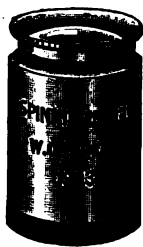
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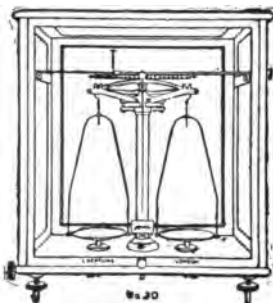
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2283.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 86).

CHAPTER I. (continued).

Measurement of the Intensity of Radiation.

THE method employed consists in measuring the conductivity acquired by air under the action of radio-active bodies; this method possesses the advantage of being rapid and of furnishing figures which are comparable. The apparatus employed by me for the purpose consists essentially of a plate condenser, A B (Fig. 1). The active

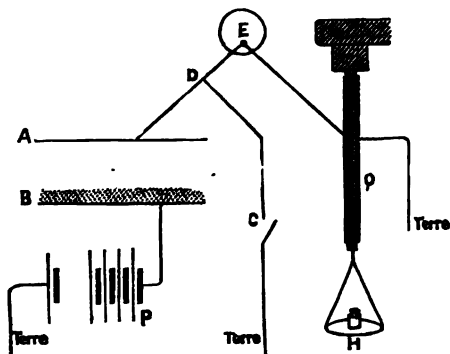


FIG. 1.

body, finely powdered, is spread over the plate B, making the air between the plates a conductor. In order to measure the conductivity, the plate B is raised to a high potential by connecting it with one pole of a battery of small accumulators, P, of which the other pole is connected to earth. The plate A being maintained at the potential of the earth by the connection C D, an electric current is set up between the two plates. The potential of plate A is recorded by an electrometer, E. If the earth connection be broken at C, the plate A becomes charged, and this charge causes a deflection of the electrometer. The velocity of the deflection is proportional to the intensity of the current, and serves to measure the latter.

But a preferable method of measurement is that of compensating the charge on plate A, so as to cause no deflection of the electrometer. The charges in question are extremely weak; they may be compensated by means of a quartz electric balance, Q, one sheath of which is connected to plate A and the other to earth. The quartz lamina is subjected to a known tension, produced by placing weights in a plate, π ; the tension is produced progressively, and has the effect of generating progressively a known quantity of electricity during the time observed. The operation can be so regulated that, at each instant, there is compensation between the quantity of electricity that traverses the condenser and that of the opposite kind furnished by the quartz. In this way, the quantity of electricity passing through the condenser for a given time, i.e., the intensity of the current, can be measured in absolute units. The measurement is independent of the sensitiveness of the electrometer.

In carrying out a certain number of measurements of this kind, it is seen that radio-activity is a phenomenon capable

of being measured with a certain accuracy. It varies little with temperature; it is scarcely affected by variations in the temperature of the surroundings; it is not influenced by incandescence of the active substance. The intensity of the current which traverses the condenser increases with the surface of the plates. For a given condenser and a given substance the current increases with the difference of potential between the plates, with the pressure of the gas which fills the condenser, and with the distance of the plates (provided this distance be not too great in comparison with the diameter). In every case, for great differences of potential the current attains a limiting value, which is practically constant. This is the *current of saturation*, or *limiting current*. Similarly, for a certain sufficiently great distance between the plates the current hardly varies any longer with the distance. It is the current obtained under these conditions that was taken as the measure of radio-activity in my researches, the condenser being placed in air at atmospheric pressure.

I append curves which represent the intensity of the current as a function of the field established between the plates for two different plate distances. Plate B was covered with a thin layer of powdered metallic uranium; plate A, connected with the electrometer, was provided with a guard-ring.

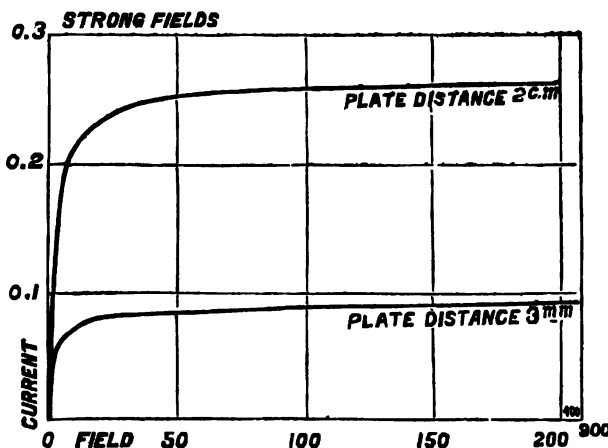


Fig. 2.

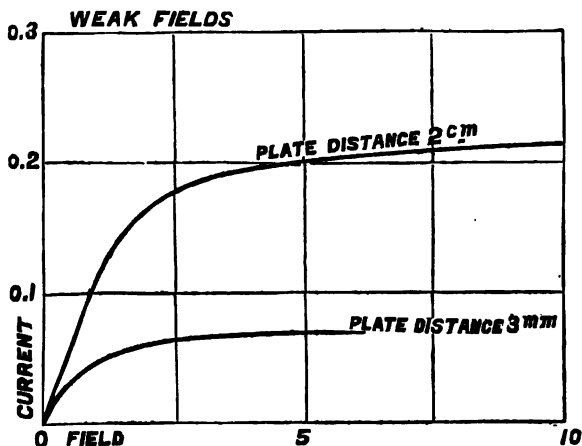


Fig. 3.

Fig. 2 shows that the intensity of the current becomes constant for high potential differences between the plates. Fig. 3 represents the same curves on another scale, and

* Thesis presented to the Faculté des Sciences de Paris.

comprehends only relative results for small differences of potential. At the origin, the curve is rectilinear; the ratio of the intensity of the current to the difference of potential is constant for weak forces, and represents the initial conduction between the plates. Two important characteristic constants of the observed phenomenon are therefore to be recognised:—(1) The *initial conduction* for small differences of potential; (2) the *limiting current* for great potential differences. The limiting current has been adopted as the measure of the radio-activity.

Besides the difference of potential established between the two plates, there exists between them an electromotive force of contact, and these two sources of current combine their effects; for this reason, the absolute value of the intensity of the current changes with the sign of the external difference of potential. In every case, for considerable potential differences, the effect of the electromotive force of contact is negligible, and the intensity of the current is therefore the same whatever be the direction of the field between the plates.

The investigation of the conductivity of air and other gases subjected to the action of Becquerel rays has been undertaken by several physicists. A very complete research upon the subject has been published by Mr. Rutherford.

The laws of the conductivity produced in gases by the Becquerel rays are the same as those found for the Röntgen rays. The mechanics of the phenomenon appear to be the same in both cases. The theory of ionisation of the gases by the action of the Röntgen or Becquerel rays agrees well with the observed facts. This theory will not be put forward here. I will merely record the results to which they point:—

Firstly, the number of ions produced per second in the gas is considered proportional to the energy of radiation absorbed by the gas.

Secondly, in order to obtain the limiting current relatively to a given radiation, it is necessary, on the one hand, to cause complete absorption of this radiation by the gas by employing a sufficient mass of it; on the other hand, it is necessary for the production of the current to use all the ions generated by establishing an electric field of such strength that the number of the ions which recombine may be a negligible fraction of the total number of ions produced in the same time, most of which are carried by the current to the electrodes. The strength of the electric field necessary to give this result is proportional to the amount of ionisation.

According to the recent researches of Mr. Townsend, the phenomenon is more complex when the pressure of the gas is low. At first the current appears to approach to a constant limiting value with increasing difference of potential; but after a certain point has been reached, the current begins again to increase with the field, and with very great rapidity. Mr. Townsend ascribes this increase to a new ionisation produced by the ions themselves when, under the action of the electric field, they acquire a velocity such that a molecule of gas encountering one of them becomes broken down into its constituent ions. A strong electric field and a low pressure are favourable to the production of this ionisation by ions already present, and, as soon as the action is set up, the intensity of the current increases uniformly with the field between the plates. The limiting current could, therefore, only be obtained under conditions of ionisation of which the intensity does not exceed a certain value, and in such a manner that saturation corresponds to fields in which, from multiplicity of ions, ionisation can no longer take place. This condition has occurred in my experiments.

The order of magnitude of the saturation currents obtained with uranium compounds is 10^{-11} ampères for a condenser in which the plates have a diameter of 8 c.m., and are at a distance of 3 c.m. Thorium compounds give rise to currents of the same order of magnitude, and the activity of the oxides of uranium and thorium is very similar.

Radio-activity of the Compounds of Uranium and Thorium.

The following are the figures I obtained with different uranium compounds. I have represented the intensity of the current in ampères by the letter *i*:—

	$i \times 10^{11}$
Metallic uranium (containing a little carbon)	2.3
Black oxide of uranium, U_2O_5	2.6
Green " " U_3O_4	1.8
Hydrated uranic acid	0.6
Uranate of sodium	1.2
" potassium	1.2
" ammonium	1.3
Uranium sulphate	0.7
Sulphate of uranium and potassium	0.7
Nitrate of uranium	0.7
Phosphate of copper and uranium	0.9
Oxysulphide of uranium	1.2

The thickness of the layer of the uranium compound used has little effect, provided that the layer is uniform. The following illustrate this point:—

	Thickness of layer.	$i \times 10^{11}$
	M.m.	
Uranium oxide	0.5	2.7
" "	3.0	3.0
Ammonium uranate	0.5	1.3
" "	3.0	1.4

It may be concluded from this that the absorption of uranium rays by the substance which generates them is very great, since the rays proceeding from deep layers produce no significant effect.

The figures I obtained with thorium compounds enable me to state:—

Firstly, that the thickness of the layer used has considerable effect, especially in the case of the oxide.

Secondly, that the action is only regular if a sufficiently thin layer is used (e.g., 0.25 m.m.). On the contrary, when a thick layer of the substance is used (6 m.m.), the figures obtained vary between two extreme limits, especially in the case of the oxide:—

	Thickness of layer.	$i \times 10^{11}$
	M.m.	
Thorium oxide	0.25	2.2
" "	0.5	2.5
" "	2.5	4.7
" "	3.0	5.5 (mean)
" "	6.0	5.5
Thorium sulphate	0.25	0.8

There is here some cause of irregularities which do not exist in the case of the uranium compounds. The figures obtained for a layer of oxide 6 m.m. thick varied between 3.7 and 7.3.

The experiments that I made on the absorption of uranium and thorium rays showed that those of thorium are more penetrating than those of uranium, and that the rays emitted by the oxide of thorium in a thick layer are more penetrating than those emitted by a thin layer of the same. The following figures give the fraction of the radiation transmitted by a sheet of aluminium 0.01 thick:—

Radio-active substance.	Fraction of radiation transmitted by the sheet.
Uranium	0.18
Uranium oxide, U_2O_5	0.20
Uranate of ammonium	0.20
Phosphate of uranium and copper	0.21
Thorium oxide of thickness 0.25 m.m.	0.38
" "	0.5
" "	3.0
" "	6.0
Thorium sulphate	0.25

With the uranium compounds, the absorption is the same whatever be the compound used, which leads to the

conclusion that the rays emitted by the different compounds are of the same nature.

The characteristics of the thorium radiation have formed the subject of very complete publications. Mr. Owens has demonstrated that a uniform current is only obtained after some time has elapsed, with an enclosed apparatus, and that the intensity of the current is greatly reduced under the influence of a current of air (which does not occur with the compounds of uranium). Mr. Rutherford has made similar experiments, and has explained them by the proposition that thorium and its compounds produce, besides the Becquerel rays, another emanation, composed of extremely minute particles, which remain radio-active for some time after their emission, and are capable of being swept along by a current of air.

The characteristics of the thorium radiation, which have reference to the thickness of the layer employed and to the action of air currents, have an intimate connection with the phenomenon of the radio-activity induced, and of its propagation from place to place. This phenomenon was observed for the first time with radium, and will be described later.

The radio-activity of thorium and uranium compounds appears as an atomic property. M. Becquerel had already observed that all uranium compounds are active, and had concluded that their activity was due to the presence of the element uranium; he also demonstrated that uranium was more active than its salts. I have investigated, from this point of view, the compounds of thorium and uranium, and have taken a great many measurements of their activity under different conditions. The result of all these determinations shows the radio-activity of these substances to be decidedly an atomic property. It seems to depend upon the presence of atoms of the two elements in question, and is not influenced by any change of physical state or chemical decomposition. The chemical combinations and mixtures containing uranium or thorium are active in proportion to the amount of the metal contained, all inactive material acting as inert bodies and absorbing the radiation.

Is Atomic Radio-activity a general Phenomenon?

As I have said above, I made experiments to discover whether substances other than compounds of uranium and thorium were radio-active. I undertook this research with the idea that it was scarcely probable that radio-activity, considered as an atomic property, should belong to a certain kind of matter to the exclusion of all other. The determinations I made permit me to say that, for chemical elements actually considered as such, including the rarest and most hypothetical, the compounds I investigated were always at least 100 times less active in my apparatus than metallic uranium.

The following is a summary of the substances experimented upon, either as the element or in combination:—

1. All the metals or non-metals easily procurable, and some, more rare, pure products obtained from the collection of M. Etard, at the Ecole de Physique et de Chimie Industrielles de la Ville de Paris.

2. The following rare bodies:—Gallium, germanium, neodymium, praseodymium, niobium, scandium, gadolinium, erbium, samarium, and rubidium (specimens lent by M. Demarçay), yttrium, ytterbium (lent by M. Urbain).

3. A large number of rocks and minerals.

Within the limits of sensitiveness of any apparatus, I found no simple substance, other than uranium and thorium, possessing atomic radio-activity. It will be suitable to add a few words here concerning phosphorus. White moist phosphorus, placed between the plates of the condenser, causes the air between the plates to conduct. However, I do not consider this body radio-active in the same manner as thorium and uranium. For, under these conditions, phosphorus becomes oxidised and emits luminous rays, whilst uranium and thorium compounds are radio-active without showing any chemical change which can be detected by any known means. Further, phosphorus

is not active in the red variety, nor in a state of combination.

In a recent work, M. Bloch has demonstrated that phosphorus, undergoing oxidation in air, gives rise to slightly motile ions, which make the air conduct, and cause condensation of aqueous vapour.

Uranium and thorium are elements which possess the highest atomic weights (240 and 232); they occur frequently in the same minerals.

Radio-active Minerals.

I have examined many minerals in my apparatus; certain of them gave evidence of radio-activity, e.g., pitchblende, thorite, orangite, fergusonite, cleveite, chalcilite, autunite, monazite, &c. The following is a table giving in ampères the intensity, *i*, of the current obtained with metallic uranium and with different minerals:—

	$\times 10^{11}$
Uranium	2.3
Pitchblende from Johanngeorgenstadt	8.3
" " Joachimsthal	7.0
" " Pzibran	6.5
" " Cornwallis	1.6
Cleveite	1.4
Chalcilite	5.2
Autunite	2.7
Various thorites	0.1 0.3 0.7 1.3 1.4
Orangite	2.0
Monazite	0.5
Xenotime	0.03
Æschynite	0.7
Fergusonite (two samples)	0.4 0.1
Samaraskite	1.1
Niobite (two samples)	0.1 0.3
Tantalite	0.02
Carnotite	6.2

The current obtained with orangite (native oxide of thorium) varied greatly with the thickness of the layer. By increasing this thickness from 0.25 m.m. to 6 m.m. the current increased from 1.8 to 2.3.

All the minerals which showed radio-activity contained uranium or thorium; their activity is therefore not surprising, but the intensity of the action in certain cases is unexpected. Thus pitchblendes (ores of uranium oxide) are found which are four times as active as metallic uranium. Chalcilite (double phosphate of copper and uranium) is twice as active as uranium. Autunite (phosphate of uranium and calcium) is as active as uranium. These facts did not accord with previous conclusions, according to which no mineral should be so active as thorium or uranium.

To throw light on this point, I prepared artificial chalcilite by the process of Debray, starting with the pure products. The process consists in mixing a solution of uranium nitrate with a solution of copper phosphate in phosphoric acid and warming to 50° or 60°. After some time, crystals of chalcilite appear in the liquid.

Chalcilite thus obtained possesses a perfectly normal activity, given by its composition; it is two and a-half times less active than uranium.

It therefore appeared probable that if pitchblende, chalcilite, and autunite possess so great a degree of activity, these substances contain a small quantity of a strongly radio-active body, differing from uranium and thorium and the simple bodies actually known. I thought that if this were indeed the case, I might hope to extract this substance from the ore by the ordinary methods of chemical analysis.

(To be continued).

EXPERIMENTS IN RADIO-ACTIVITY, AND THE PRODUCTION OF HELIUM FROM RADIUM.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.,
and
FREDERICK SODDY, M.A.1. *Experiments on the Radio-activity of the Inert Gases of the Atmosphere.*

OF recent years many investigations have been made by Elster and Geitel, Wilson, Strutt, Rutherford, Cooke, Allen, and others, on the spontaneous ionisation of the gases of the atmosphere, and on the excited radio-activity obtainable from it. It became of interest to ascertain whether the inert monatomic gases of the atmosphere bear any share in these phenomena. For this purpose a small electro-scope contained in a glass tube of about 20 c.c. capacity, covered in the interior with tin-foil, was employed. After charging, the apparatus, if exhausted, retained its charge for thirty-six hours without diminution. Admission of air caused a slow discharge. In similar experiments with helium, neon, argon, krypton, and xenon, the last mixed with oxygen, the rate of discharge was proportional to the density and pressure of the gas. This shows that the gases have no special radio-activity of their own, and accords with the explanation already advanced by these investigators, that the discharging power of the air is caused by extraneous radio-activity.

Experiments were also made with the dregs left after liquefied air had nearly entirely evaporated, and again with the same result; no increase in discharging power is produced by concentration of a possible radio-active constituent of the atmosphere.

2. *Experiments on the Nature of the Radio-active Emanation from Radium.*

The word emanation originally used by Boyle ("substantial emanations from the celestial bodies") was resuscitated by Rutherford to designate definite substances of a gaseous nature, continuously produced from other substances. The term was also used by Russell ("emanation from hydrogen peroxide") in much the same sense. If the adjective "radio-active" be added, the phenomenon of Rutherford is distinguished from the phenomena observed by Russell. In this section we are dealing with the emanation, or radio-active gas obtained from radium. Rutherford and Soddy investigated the chemical nature of the thorium emanation (*Phil. Mag.*, 1902, p. 580), and of the radium emanation (*Phil. Mag.*, 1903, p. 457), and came to the conclusion that these emanations are inert gases which withstand the action of reagents in a manner hitherto unobserved, except with the members of the argon family. This conclusion was arrived at because the emanations from thorium and radium could be passed without alteration over platinum and palladium black, chromate of lead, zinc dust, and magnesium powder, all at a red heat.

We have since found that the radium emanation withstands prolonged sparking with oxygen over alkali, and also, during several hours, the action of a heated mixture of magnesium powder and lime. The discharging power was maintained unaltered after this treatment, and inasmuch as a considerable amount of radium was employed, it was possible to use the self-luminosity of the gas as an optical demonstration of its persistence.

In an experiment in which the emanation mixed with oxygen had been sparked for several hours over alkali, a minute fraction of the total mixture was found to discharge an electro-scope almost instantly. From the main quantity of the gas, the oxygen was withdrawn by ignited phosphorus, and no visible residue was left. When, however, another gas was introduced, so as to come into contact with the top of the tube, and then withdrawn, the emanation was found to be present in it in unaltered amount. It appears, therefore, that phosphorus burning in oxygen and sparking with oxygen have no effect upon the gas so far as can be detected by its radio-active properties.

* A Paper communicated to the Royal Society, July 28, 1903.

The experiments with magnesium-lime were more strictly quantitative. The method of testing the gas before and after treatment with the reagent was to take 1/2000 part of the whole mixed with air, and after introducing it into the reservoir of an electro-scope to measure the rate of discharge. The magnesium-lime tube glowed brightly when the mixture of emanation and air was admitted, and it was maintained at a red heat for three hours. The gas was then washed out with a little hydrogen, diluted with air and tested as before. It was found that the discharging power of the gas had been quite unaltered by this treatment.

The emanation can be dealt with as a gas; it can be extracted by aid of a Töpler pump; it can be condensed in a U-tube surrounded by liquid air, and when condensed it can be "washed" with another gas, which can be pumped off completely, and which then possesses no luminosity and practically no discharging power. The passage of the emanation from place to place through glass tubes can be followed by the eye in a darkened room. On opening a stopcock between a tube containing the emanation and the pump, the slow flow through the capillary tube can be noticed; the rapid passage along the wider tubes, the delay caused by the plug of phosphorus pentoxide, and the sudden diffusion into the reservoir of the pump. When compressed, the luminosity increased, and when the small bubble was expelled through the capillary it was exceedingly luminous. The peculiarities of the excited activity left behind on the glass by the emanation could also be well observed. When the emanation had been left a short time in contact with the glass, the excited activity lasts only for a short time; but after the emanation has been stored a long time the excited activity decays more slowly.

The emanation causes chemical change in a similar manner to the salts of radium themselves. The emanation pumped off from 50 m.grms. of radium bromide after dissolving in water, when stored with oxygen in a small glass tube over mercury, turns the glass distinctly violet in a single night; if moist, the mercury becomes covered with a film of the red oxide, but if dry, it appears to remain unattacked. A mixture of the emanation with oxygen produces carbon dioxide when passed through a lubricated stopcock.

3. *Occurrence of Helium in the Gases Evolved from Radium Bromide.*

The gas evolved from 20 m.grms. of pure radium bromide (which we are informed had been prepared three months) by its solution in water, and which consisted mainly of hydrogen and oxygen (*cf. Giesel, Ber.*, 1903, 347) was tested for helium, the hydrogen and oxygen being removed by contact with a red-hot spiral of copper wire, partially oxidised, and the resulting water vapour by a tube of phosphorus pentoxide. The gas issued into a small vacuum tube which showed the spectrum of carbon dioxide. The vacuum tube was in train with a small U-tube, and the latter was then cooled with liquid air. This much reduced the brilliancy of the CO₂ spectrum, and the D₃ line of helium appeared. The coincidence was confirmed by throwing the spectrum of helium into the spectro-scope through the comparison prism, and shown to be at least within 0.5 of an Angström unit.

The experiment was carefully repeated in apparatus constructed of previously unused glass with 30 m.grms. of radium bromide, probably four or five months old, kindly lent us by Prof. Rutherford. The gases evolved were passed through a cooled U-tube on their way to the vacuum tube, which completely prevented the passage of carbon dioxide and the emanation. The spectrum of helium was obtained, and practically all the lines were seen, including those at 6677, 5876, 5016, 4932, 4713, and 4472. There were also present three lines of approximate wave-lengths, 6180, 5695, 5455, that have not yet been identified.

On two subsequent occasions, the gases evolved from both solutions of radium bromide were mixed, after four days' accumulation, which amounted to about 2.5 c.c. in

each case, and were examined in a similar way. The D₃ line of helium could not be detected. It may be well to state the composition found for the gases continuously generated by a solution of radium, for it seemed likely that the large excess of hydrogen over the composition required to form water, shown in the analysis given by Böldlander (*Ber., loc. cit.*) might be due to the greater solubility of the oxygen. In our analyses the gases were extracted with the pump, and the first gave 28.6, the second 29.2 per cent of oxygen. The slight excess of hydrogen is doubtless due to the action of the oxygen on the grease of the stopcocks, which has been already mentioned. The rate of production of these gases is about 0.5 c.c. per day for 50 m.grms. of radium bromide, which is over twice as great as that found by Böldlander.

4. Production of Helium by the Radium Emanation.

The maximum amount of the emanation obtained from 50 m.grms. of radium bromide was conveyed by means of oxygen into a U-tube cooled in liquid air, and the latter was then extracted by the pump. It was then washed out with a little fresh oxygen, which was again pumped off. The vacuum tube sealed on to the U-tube, after removing the liquid air, showed no trace of helium. The spectrum was apparently a new one, probably that of the emanation, but this has not yet been completely examined, and we hope to publish further details shortly. After standing from the 17th to the 21st inst., the helium spectrum appeared, and the characteristic lines were observed identical in position with those of a helium tube thrown into the field of vision at the same time. On the 22nd, the yellow, the green, the two blues, and the violet, were seen, and in addition the three new lines also present in the helium obtained from radium. A confirmatory experiment gave identical results.

We wish to express our indebtedness to the Research Fund of the Chemical Society for a part of the radium used in this investigation.

ON THE

INTENSELY PENETRATING RAYS OF RADIUM.*

By Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge.

RADIUM is known to emit three types of radiation. These are—

1. The α -rays, very easily absorbed by solids, and carrying a positive electric charge.
2. The β -rays, more penetrating than these, and negatively charged.
3. The γ -rays, intensely penetrating, and not conveying an electric charge at all.

In a paper published in the *Phil. Trans.* for 1901, I investigated the relative ionisations of gases by the α - and β -rays. The present communication may be regarded as a sequel to that one, and deals with the γ -rays.

The radium employed was of activity 1000 (uranium = 1), and was contained in a glass cell, over which was cemented a piece of thin aluminium. The cell was placed in a cavity in a block of lead, and over it was placed a disc of lead 1 c.m. in thickness. This it was considered would suffice to suppress all but the γ -rays, which are much the most penetrating.

In measuring the electrical leakage, the electroscope method was employed. The apparatus was that described in a paper published in the *Philosophical Magazine* for June, 1903, p. 681.

The radium, covered by the thick lead, was placed under the apparatus, and the rate of leak determined when the different gases filled the testing vessel.

The conditions were, of course, arranged so as to use a saturating E.M.F. The γ -rays are so penetrating that there can be no question of their being appreciably absorbed in a moderate thickness of gas.

For the methods of preparation of the gases I must refer to the former paper (*Phil. Trans.*, A., 1901, vol. cxcvi., p. 508).

The results were as follows; the rates of leak are given in scale divisions per hour, and are corrected to 30 inches pressure:—

Gas.	Rate of leak.	Mean.
Hydrogen	10.4, 10.5, 10.4, 11.2, 10.4, 11.2, 9.86, 10.1, 10.2 ..	10.5
Air	65.2, 66.6, 66.6, 60.0, 57.0, 61.5, 60.2, 63.0, 58.2, 58.3, 56.6, 56.2 ..	62.1
Oxygen	75.0, 74.2, 71.0, 74.1 ..	73.6
Carbon dioxide ..	96.0, 95.4, 94.5, 95.1, 94.1, 94.7 ..	95.0
Cyanogen	107, 104, 106, 106 ..	106.0
Sulphur dioxide ..	132, 126, 134, 135 ..	132.0
Chloroform	297, 298, 290, 327 ..	303.0
Methyl iodide ..	298, 292, 310, 291 ..	298.0
Carbon tetrachloride.	363, 351, 344, 349 ..	352.0

The following table gives the relative ionisations, referred to air as unity. The values of the same constants for the α - and β -rays formerly found are included, and also measurements of relative ionisation under Röntgen rays. These latter form part of an investigation now hitherto published:—

Relative Ionisations.

Gas.	Relative density.	Relative ionisation.			
		α -Rays.	β -Rays.	γ -Rays.	Röntgen rays.
Hydrogen ..	0.0693	0.226	0.157	0.169	0.114
Air	1.00	1.00	1.00	1.00	1.00
Oxygen ..	1.11	1.16	1.21	1.17	1.39
Carbon dioxide	1.53	1.54	1.57	1.53	1.60
Cyanogen ..	1.86	1.94	1.86	1.71	1.05
Sulphur dioxide	2.19	2.04	2.31	2.13	7.97
Chloroform ..	4.32	4.44	4.89	4.88	31.9
Methyl iodide	5.05	3.51	5.18	4.80	72.0
Carbon tetra-chloride ..	5.31	5.34	5.83	5.67	45.3

The determinations for the γ -rays are less accurate than the former ones for the α - and β -rays, on account of the very much smaller rates of leak which have to be measured. I think, if this be taken into account, there is no reason to doubt that, within the limits of experimental error, the γ -rays give the same values as the β -rays. These values are nearly proportional to the density of the gas, except in the case of hydrogen. The law which holds in the case of Röntgen rays is totally different.

This conclusion throws some light on the nature of the γ -rays. The view seems to be gaining ground that these are Röntgen rays, produced by the impact of the β -rays on the radium itself (see, for instance, M^{me}. Curie, "Thèses présentées à la Faculté des Sciences," 1903, p. 83; *CHEM. NEWS*, vol. lxxxviii., p. 85 *et seq.*). This theory seems to have much to recommend it. The β rays should, by analogy with the cathode rays in a vacuum tube, produce Röntgen rays when they strike a solid obstacle, and these Röntgen rays should be much more penetrating than the β -rays themselves. The γ -rays seem at first sight to be just what should be expected. But the present paper shows that, in one respect at all events, the γ -rays behave quite differently to Röntgen rays, while, on the other hand, they resemble the α - and β -rays. There seems to be a possibility that they, too, are of a corpuscular nature, though uncharged with electricity. This would account for the absence of magnetic deflection.

I do not think that the absence of conspicuous Röntgen radiation is very hard to understand, if we consider that the current emitted in cathode rays by a square inch of intensely active radium is only 10^{-11} ampères; the current through a focus tube is of the order 10^{-2} ampères, and probably a great part of this is carried by the cathode rays.

* A Paper communicated to the Royal Society, August 5, 1903.

ELECTROLYTIC APPARATUS.*

By F. MOLLWO PERKIN, Ph.D.

Owing to the great expense of platinum and the necessity for its use in electro-chemical analysis, members may be interested in the description of a simple form of electrode, which is comparatively inexpensive and is very satisfactory.

In Fig. 1, which shows the electrodes, the cathode is in the form of a flag, and is made of platinum gauze, which is held rigid by means of a platino-iridium frame (10 per cent iridium); the frame, which is roughened by means of the sand-blast, has a stout piece of iridio-platinum wire welded on to it. The wire, of course, is for holding the electrode in position during analysis. The loop near the top of the wire is for hanging the electrode on the balance. The anode is made of iridio-platinum wire, and is bent upon itself in such a way that when it is placed into position for electrolysis, as illustrated in Fig. 2, an even current density is obtained on all parts of the cathode. The distance between the two sides of the anode is 2.5 c.m., therefore when in position it is 1.25 c.m. distant from each side of the cathode.

The cathode is 6 c.m. high and 4.3 c.m. wide, and the length of the supporting wire is 7.5 c.m., the loop being 2.5 c.m. from the end. As the anode is opposed to both sides of the cathode during electrolysis, it follows from the above measurements that the total cathode surface is 50.4 c.m.², that is practically half a square decimetre, which, as the C.D. for analytical purposes is generally calculated per square decimetre of surface, is a very convenient size. It is not essential for the cathode to be made of gauze—in

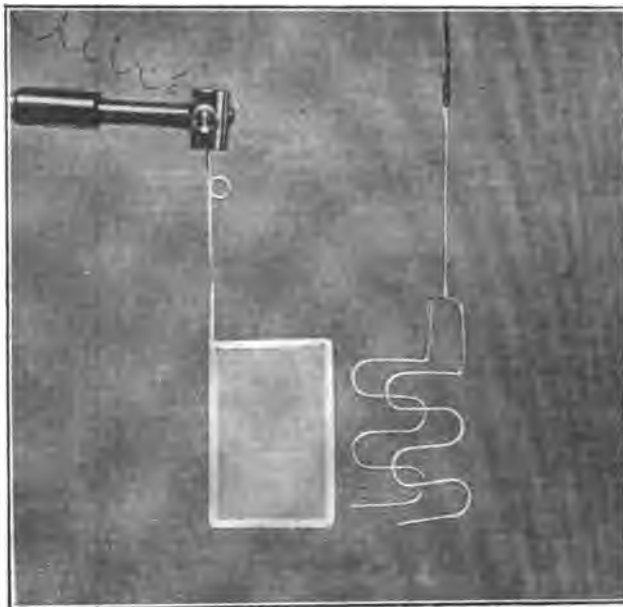


FIG. 1.

many cases sheet platinum is quite as useful; but for metallic deposits which are inclined to exfoliate, such as bismuth and antimony, the gauze is more satisfactory; it is also very useful for mercury and for peroxide deposits. The gauze should not be too fine; the finest which I have found satisfactory is about 50 to 60 meshes to the square

* A Paper read before the Faraday Society, June 30, 1903.

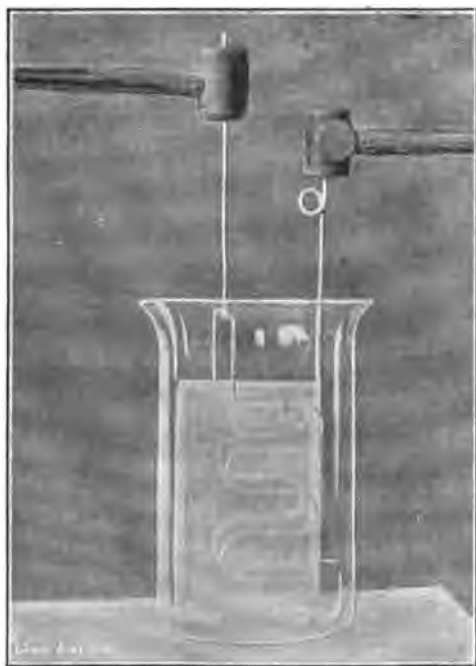


FIG. 2.

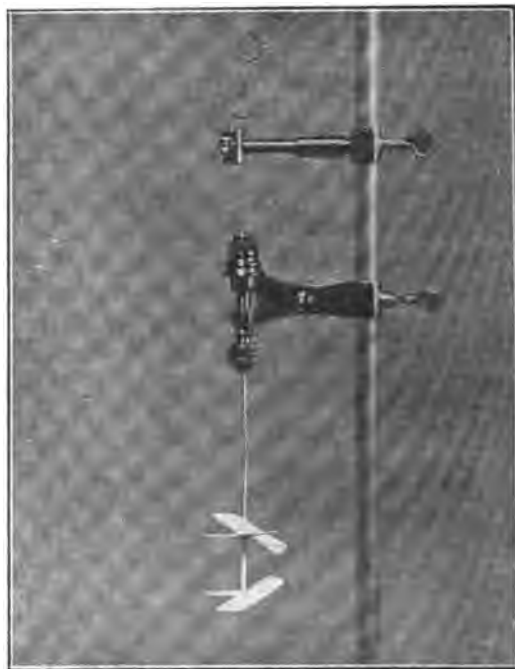


FIG. 3.

centimetre. When it is too fine there is a tendency for hydrogen to collect upon the surface and thus cause polarisation.

The weight of the cathode, when made of platinum sheet, is about 14.5 grms. If thinner platinum is employed the weight can be reduced to 8 grms., but I have found it better not to make them of very thin platinum, because then they are fragile, and there is a tendency for the deposits not to adhere well at the edges. The weight of the gauze electrode is about 15 grms. It follows that, as these electrodes weigh much less than the basin or cylinder ones, they are much cheaper. A basin usually weighs from 45 to 60 grms., and a cylinder from 26 to 28 grms.

These electrodes are also more satisfactory for carrying out electrolytic separations, the manipulation being much easier than with the basin. Suppose, *e.g.*, that one is electrolysing a mixture of copper and iron salts. In the first place the copper would be deposited out from an acid solution; then, after neutralising, the iron would be electrolysed out. Now when a basin is used, the solution has to be transferred to a beaker, and, as the manipulation has to be rapid, there is a danger of loss through spilling; further, the acid solution must not be left in contact with the copper deposit. The dish therefore must be washed at once, and the solution which is clinging to its sides, and which contains iron, is lost. In the case of the flag electrode, the cathode is rapidly raised out of the beaker and the solution at once washed off its sides, while it is hanging over the top of the beaker, by means of a wash-bottle. The solution in the beaker can then be neutralised without being transferred to another vessel; multiplication of manipulation is thus avoided.



FIG. 4.

Apparatus for Rotating Electrodes.

It is often necessary in electrolysis to keep the electrolyte agitated. This is generally done by means of an agitator, entirely separated from the electrodes and rotated by means of a water-turbine or motor. In many cases, however, much better results are obtained if one of the electrodes is itself caused to rotate. In most of the descriptions of rotating electrodes, there seems to have been considerable difficulty in obtaining good electrical contact, and the methods employed have often been rather complicated. Fig. 3 shows an arrangement which has been found to work extremely well.

It consists of a supporting arm, made of gun-metal, the end of which is drilled to allow a spindle to pass. This spindle carries a small chuck (such as is used for fixing small drills on a lathe) which is used for fixing the rotator. The grooved pulley, which is fastened on to the upper end of the spindle, bears on the top of the arm, which is ground smooth. The whole arrangement is driven by means of a belt from a water-turbine or electrical motor. This arrangement is found to give very perfect contact and to work with very little friction. The parts should only be slightly lubricated, the best lubricant being a mixture of graphite and vaseline. The water-turbine, which has proved very useful and has been working for a long time, has ball bearings—an unusual nicety—and was obtained from Messrs. Baird and Tatlock, Glasgow.

Fig. 4 shows another form of the rotator, which can be driven either from a horizontal or vertical pulley, and is also convenient for working several apparatus in series. The electrode shown in Fig. 3 is of iridium-platinum, and has been used with very satisfactory results in the electrical

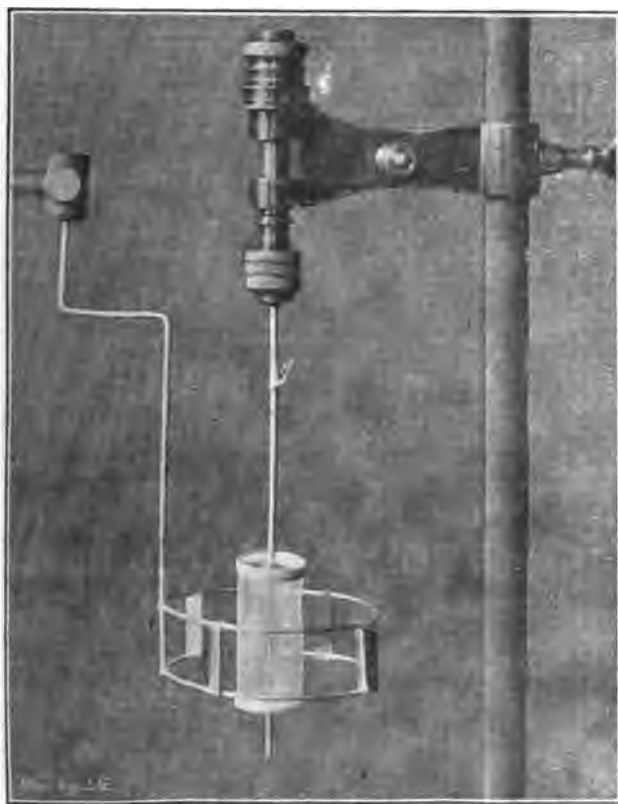


FIG. 5.

oxidation of organic substances. The electrode in Fig. 4 is of aluminium.

I have found the following method work very well for making rotating lead electrodes. Thin lead pipe, to which the vanes for mixing the liquid are burned, is drawn over a steel rod of the same diameter as the bore of the pipe. The steel rod protrudes about an inch above the top of the pipe, in order that it may be fastened in the chuck. The pipe is burned at the bottom and the top to prevent the solution from running in between it and the steel core. If a central core such as this is not used, lead electrodes are not sufficiently rigid to use for rotating purposes.

Rotating Cathode for Analysis.

In Fig. 5 is shown a rotating cathode and a stationary anode for electrolytic depositions. It is found that the rate of deposition of a metal from its solutions is very much accelerated and that a higher C.D. can be employed when the cathode is kept in rapid motion. The cathode is a small cylinder of platinum gauze which has a combined surface of about 25 c.m.². The anode B is in the form of a double circle of stout platinum wire, and has four little baffles placed at intervals round it to prevent the liquid from rotating with the cathode. Of course, for peroxide deposits the rotating electrode would be the anode. A cylinder of sheet platinum also gives very good results, but in this case very little metal is deposited upon the inner surface. Longitudinal slits, however, partially get over this difficulty, but with gauze as shown in the figure the deposition is practically equal inside and outside.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 218 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 218 samples examined by us during the month, 216 were found to be clear, bright, and well filtered; and two samples were recorded as slightly turbid.

The rainfall at Oxford during July, though above the average, is considerably less than that recorded during June. The actual fall has been 3.47 inches; the average for the month is 2.49 inches; this gives an excess of 0.98 inch, which, added to the previous one of 7.83 inches, makes a total excess for the year of 8.81 inches, which is 66.2 per cent above the thirty-five years' average.

The results of the chemical examination of the London waters during the month of July show that the soluble

organic matter in the average supply has considerably diminished, and that the general character of the unfiltered Thames water is now approaching that which is generally typical of its composition during the summer months.

Our bacteriological examinations of 387 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 317 others from special wells, standpipes, &c., making a total of 704 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	258
New River, filtered (mean of 81 samples) ..	11
Thames, unfiltered (mean of 27 samples) ..	3805
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples) ..	23
Ditto ditto highest	250
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	261
River Lea, from the East London Water Company's clear-water wells (mean of 26 samples)	36

Of the 307 daily samples taken from the filter wells of the Metropolitan Water Companies, nineteen, or 6.1 per cent, were sterile. There were ten samples, or 3.2 per cent, containing more than 100 microbes, and of these, four samples contained more than 150 microbes per c.c. The ten excess samples contained an average of 159 microbes per c.c.; in June fifteen excess samples contained an average of 247 microbes per c.c. The above results show a great improvement in the bacteriological quality of the water during the past month. The natural unfiltered Thames water has improved bacteriologically about 50 per cent, and the supply may now be said to be approaching its normal summer condition.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

LIQUID BATHS FOR MELTING-POINT DETERMINATIONS.

By HEYWARD SCUDDER.

A MIXTURE prepared by boiling together for five minutes seven parts by weight of sulphuric acid (sp. gr. 1.84) and three parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures, and can be heated up to 325° without boiling. If the proportions are changed to six parts by weight of acid and four parts of the sulphate, the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half-an-hour or more) melting from 60–100° and boiling above 365°. Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing, and remain permanently white (turning slightly yellowish at about 230°) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapour is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 c.m. above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted the two layers should be mixed, or explosive boiling may occur.

Most melting-points given accurately are below 325°. The first mixture is therefore suitable for all ordinary purposes. It does not have to be renewed frequently as does the ordinary sulphuric acid bath, nor does it become per-

manently discoloured as does paraffin after short use, even though prepared by distillation under diminished pressure.

If the bath has solidified (which happens sometimes under unknown conditions, though very rarely), boiling for for a minute or two will bring it back to its original condition. If it has not been used for a number of weeks, it should be boiled for a minute or two before using for temperatures above 300°.

For temperatures from 360° to 600° Mr. Booth, working under the direction of Dr. Mulliken of this laboratory, has found that the most satisfactory bath is fused zinc chloride. This melts to a clear transparent liquid at about 250°. After use it must be poured out on a tile while liquid, since it expands on solidification, and will crack any flask or beaker in which it is allowed to grow cold. It can be cleared from organic impurities by heating with a small crystal of potassium nitrate. Unless the zinc chloride used is pure, the bath will gradually become opaque after a short time, and cannot be made transparent again.

The temperatures given here are uncorrected. They were obtained in a melting-point apparatus made by inserting a test-tube in a round-bottom flask (150—250 c.c.). The bottom of the tube is about 1 c.m. from the bottom of the flask. The bath is placed both in the test-tube and in the flask. In this apparatus fresh sulphuric acid (sp. gr. 1.84) can be used up to 280—300°. In using the sulphate mixtures, if the upper part of the tube becomes cloudy from a film of solid, it can be cleared by boiling with a little concentrated nitric acid. In using such an apparatus it is not safe to heat it much above the temperatures given here for the various baths, since the boiling is apt to start very violently. It is safe to heat it till large bubbles begin to rise moderately frequently.

When these baths are used in open beakers, it is not possible with sulphuric acid or the sulphate mixtures to obtain temperatures as high as those previously mentioned, without having disagreeable amounts of acid vapour given off. The zinc chloride bath can be used in a beaker up to about 600°.

The sulphate mixtures seem to contain some compound in a persistent state of supersaturation. Although possessed of considerable oxidising power when hot, it is a curious fact that they are markedly less caustic than hot concentrated sulphuric acid when dropped on the skin.—*Journal of the American Chemical Society*, xxv., No. 2.

THE NATIONAL PHYSICAL LABORATORY.

REPORT BY THE DIRECTOR ON THE WORK IN THE ENGINEERING AND PHYSICS DEPARTMENTS DURING THE HALF YEAR ENDED JUNE 30, 1903.

The following statement was prepared by the Director, and laid before the Executive Committee at their Meeting on July 17th, as an interim report on the research work in progress.

The Committee, believing it would be of interest to a wider circle, ordered it to be printed and circulated.

Engineering Laboratory.

In the wind pressure research the case of flat surfaces exposed to a perpendicular current of air has been fully worked out, and a general relation established which is now being tested for the case of larger surfaces exposed to the natural wind. The case of parallel plates at varying distances apart has been treated, and experiments are also in progress on the pressure on inclined surfaces. Dr. Stanton hopes to have a paper on the results obtained at present ready for publication very shortly.

The Testing Machine for alternating stresses is nearing completion, and will, it is hoped, be ready for working in the Autumn.

Drawings have been prepared and some preliminary tests made for the research into the constants of steam.

Thermometry.

Dr. Harker has continued his comparison between the air thermometer, the platinum thermometer, and the thermojunctions, and the work is now complete for temperatures between 0° C. and about 1050° C. The first part of the work for temperatures up to 500° C. was done with M. Chappuis, at Sèvres, and the results have been published. Dr. Harker is now preparing for publication results up to temperatures of 1050° C. obtained at Bushy.

He has also constructed and subjected to stringent tests a set of platinum thermometers for the British Association.

A small research on the specific heat of iron at high temperatures—700° C. to 1000° C.—is nearly complete and promises to be of interest.

Electricity.

Mr. F. E. Smith's research on the resistance of mercury and the construction of a standard mercury resistance is practically complete. Some 10 or 12 tubes have been calibrated, and give results which will only differ among themselves by some few parts in 100,000. The value of the specific resistance of mercury will probably prove to be very close to that determined by myself and Mr. Fitzpatrick in 1888. On the assumption that the absolute value of the wire standards in the Laboratory is known, the length of the column of mercury, 1 sq. m.m. in section, having a resistance of 10⁹ C.G.S. units is found to be almost exactly 106.29 c.m.

The difference between Mr. Smith's results and those of the Reichenstalt will not be more than some few parts in 100,000.

Mr. Smith has also made good progress with a research into some of the anomalies of the Clark Cell.

An investigation of some importance into the changes in insulating strength of various dielectrics, used in motors, transformers, &c., due to continued heating, by Mr. A. Campbell and Mr. Rayner, undertaken for the Engineering Standards Committee, promises to lead to results of value.

Metallurgy.

In the Metallurgical Division preparations have been made for the work on Nickel Steel in conjunction with Mr. Hadfield; the material is being prepared by him.

Meanwhile, considerable advance has been made with a series of determinations on some iron carbon alloys.

The solidifying points and cooling curves of a series of pure iron carbon alloys have been determined, using platinum-iridium and platinum-platinum-rhodium thermojunctions. The range of carbon is from 0.15 to 3.55 per cent; the range of temperature from 1502° C. to 1111° C. on the thermojunction scale. About 15 alloys have been made, the weight of each being about 4 lbs.

The ingots have been analysed for carbon, sulphur, and silicon. The percentages of the two last named elements do not increase during the time needed for melting. Further, the ingots are satisfactorily homogeneous in composition.

The apparatus for taking cooling curves by the differential method is in working order, and the above mentioned alloys will be examined in this way.

The Director hopes that a number of important results may be published during the Autumn.

The equipment of the photometric room is approaching completion. The main photometer bench which is being standardised at the Reichenstalt has not yet been delivered.

On its arrival the Director hopes to issue a special circular giving an account of the equipment and a statement as to the conditions of the tests and the fees.

REGULATIONS FOR THE EXAMINATION OF LISTER-GERBER AND OTHER SIMILAR MILK TESTING APPARATUS.

The Committee of the National Physical Laboratory are prepared to receive, for the purpose of verification, the pipettes, measuring glasses, and test bottles used in the Lister-Gerber and other similar methods of testing milk.

The apparatus to be tested should be sent securely packed to the Director, the National Physical Laboratory, Bushy House, Teddington. The carriage to and fro must be paid by the sender. A letter of advice, which should contain the maker's name, a description of the instruments sent, and full directions for their return, must accompany all instruments sent for verification.

The Laboratory Authorities insure against damage from fire, theft, or accident, apparatus while in their custody. They also insure against risks of transit to and from the Laboratory, apparatus sent to them for testing. They will not, however, be responsible for a sum exceeding £100 on any one instrument unless a letter has been received and acknowledged by them before the instrument is sent, advising that the instrument is being sent, and requesting them to insure it for some definite sum. The value for which goods are insured is the cost price of manufacture. In all cases, a sum sufficient to cover the cost of insurance will be charged with the fees.

Limits of Accuracy.

Milk Test Bottles.—Butter and Cheese Test Bottles.—Test Bottles for Estimating the Water in Butter.

The bottles will be tested at five points on the stem graduations, and will receive the Laboratory stamp, provided—

- That the error at no point is more than 0.006 c.c.
- That the difference between the errors at any two points tested is not greater than 0.006 c.c.

Pipettes for delivering Sulphuric Acid of Specific Gravity 1.820—1.825 at 15° C.

Capacity of pipette.	Time of delivery of acid.	Permissible error.
6.5 c.c.	At least 20 seconds	0.05 c.c.
10 c.c.	" "	0.1 c.c.

Water Pipettes.

Capacity of pipette.	Time of delivery of water.	Permissible error.
8.2 c.c.	At least 30 seconds	0.02 c.c.
12 c.c.	" "	0.03 c.c.
10 c.c. divided into 1/10 c.c.	At least 30 seconds for 10 c.c.	Permissible error at any point is 0.02 c.c. The difference between the errors at any two points must not be greater than 0.02 c.c.

Amyl Alcohol Pipette.

Capacity.	Time of delivery.	Permissible error.
1 c.c.	At least 20 seconds	0.01 c.c.

Milk Pipette.

11 c.c.	At least 30 seconds	0.03 c.c.
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Cream Pipette.

3 c.c.	At least 20 seconds	0.03 c.c.
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Graduated Measuring Glasses.

These will be tested at five points.

General Conditions.

Vessels to be tested should be marked permanently with:—

- The capacity.
- The temperature at which the capacity corresponds to the mark.
- A letter or letters to indicate the purpose for which they are to be used, e.g., pipettes should bear a

letter indicative of the liquid they are intended to deliver. The abbreviations suggested are:—

- A. for acid.
A.A. for amyl alcohol.
Cr. for cream.
M. for milk.
W. for water.

Attention should be paid to the following points:—

- The cross section of that part of a vessel on which a mark is made should be circular.
- Marks must be fine, and only drawn upon cylindrical or regularly formed parts.
- The smallest distance apart of two neighbouring marks must not be less than 1 m.m.
- Marks should be sufficiently long to permit of accurate measurement.
- Vessels should be sent clean. This is ensured by first cleaning them mechanically as far as possible, next treating them with a mixture of potassium bichromate and sulphuric acid in the cold, and, lastly, rinsing them thoroughly with distilled water. An extra fee is charged if it is necessary to clean a vessel.

Stamping of Vessels Tested.

Vessels which pass the test will receive the Laboratory monogram:—

ℒ (M).

It must be clearly understood that where a pipette is stamped as correct this holds solely for the liquid it is intended to deliver, and no other. The letter (M) after the Laboratory monogram indicates that the certificate is applicable only to vessels used for milk, butter, and cream tests.

Fees.

	£	s.	d.
Test bottles, tested at five points	0	0	6
Pipettes with one mark	0	0	6
Measuring glasses with one mark	0	0	9
Graduated pipettes, tested at five points	0	1	6
Measuring glasses tested at five points	0	1	9

Instruments which fail to reach the required standard of accuracy are not marked, and half the above fee is charged.

July, 1903.

NOTE ON FILTRATION IN DETERMINATIONS OF CRUDE FIBRE.*

By R. W. THATCHER.

ALL analysts of food products, or feeding-stuffs, are familiar with the difficulty which is often experienced in filtering off the acid and the alkaline liquids in the determinations of crude fibre by the official method of the Association of Official Agricultural Chemists. Hence I wish to suggest the following modification of the usual procedure, which I have found to give very satisfactory results:—

Select a funnel of sufficient size to contain the entire bulk of the mixture to be filtered, and fit into its point a small platinum filtering cone. Introduce enough ignited asbestos-wool to fill the cone a little more than full. Upon moistening, the wool softens into a fluffy mass, which may be drawn down into a firm, close filter by suction. The mixture to be filtered is now poured into the funnel, with the usual care to avoid disturbing the asbestos layer, and suction is applied. The filtrate obtained in this manner has always been found to be free of suspended particles of fibre. Filtration is very rapid in all cases except when

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

working with finely ground flour or spices, which tend to clog the filter and impede the flow of the filtrate. In such cases place the funnel in an ordinary jacket of boiling water or steam in order to secure hot filtration, transfer the entire mass to be filtered to the funnel, and apply the suction as usual. Filtration will then proceed at the desired temperature and without further attention from the operator, thus avoiding the two objections to the use of the Gooch filter as recommended in the official method. After filtration and washing are complete, transfer the contents of the funnel to a platinum evaporating dish, rinsing the last particles of fibre from the funnel to the dish with a fine jet of distilled water. Evaporate off the water thus used, dry to constant weight, and complete the determination as usual. I prefer this mode of operation to the use of a paper filter, with correction for loss of weight sustained by the paper in a blank determination, as suggested by Winton ("Conn. Agr. Expt. Sta. Report," 1898, p. 189; and *Bull.* 65, Bur. of Chem., U.S. Dept. Agri., pp. 58, 154, and 155), for the reason that, in addition to the possibility of obtaining additional fibre from the paper used in the acid filtration, I have found that duplicate determinations of the correction to be applied do not always give concordant results, probably because of variations in the weight and composition of individual filters in any given pack of them. I have used the method outlined above for several years and upon a great variety of samples with uniformly satisfactory results. In the cases where filtration is slow it proceeds without attention from the analyst, thereby relieving the tediousness of the operation very materially.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 3, July 20, 1903.

Estimation of Traces of Arsenic.—Armand Gautier.—The new method of estimation of traces of arsenic which the author employs is of extreme simplicity, and can be used to detect minute traces of arsenic in animal organisms. The method is founded on the principle that when arsenic exists, even in very small proportion, in conjunction with iron in a mineral or potable water, the iron, when oxidised or precipitated, retains all this arsenic. The salt used is a polyferric sub-salt, and the extraction of the arsenic is so complete in this case that, under the experimental conditions which the author employs, 1/1000th of a m.grm. of arsenic, added either in the form of arsenite or arsenate to a litre of pure water is entirely removed by the iron and can be absolutely estimated.

Curves of Sublimation.—A. Bouzat.—The author showed, in a previous research, that the curves of dissociation of the group sol. $\rightleftharpoons$ sol. + gas are deduced one from the other by a very simple law. The proportion of the absolute temperatures corresponding to the same pressure in any two systems whatsoever of the group remain constant for that pressure. The vaporisation and sublimation can be deduced from the dissociation.

Law of the Re-combination of Ions.—P. Langevin.—When gases are rendered conductors of electricity, they justify in all their properties the hypothesis that the charges are carried by an infinite number of electric centres or ions—some being positive, some negative, all having the same charge in absolute value as that which transports a monovalent atom in electrolysis. The author finds that re-combination takes place when, in the relative movements of the particles, the centres of two ions at the moment of perihelion are at a distance from one another less than a constant distance, σ . The author also finds that the co-

efficient of re-combination, α , is proportional to the pressure.

Catalytic Actions of Metals.—A. Trillat.—The author investigates the catalytic action of copper and platinum with regard to oxidation, dehydrogenation, condensation, and saponification, and finds, in all cases, that the catalytic action of metals is very complex.

Ferrisulphuric Acid and Ethyl Ferrisulphate.—A. Recoura.—The author shows that ferrisulphuric acid behaves as a bibasic acid, analogous to chromosulphuric acid. He prepares ethyl ferrisulphate, and also studies the action of heat on ferrisulphuric acid.

Prussian Blue and Turnbull's Blue. A New Class of Complex Cyanides.—P. Chrétien.—Neither Prussian nor Turnbull's blue are either ferrocyanides or ferricyanides. Soluble Prussian blue has a composition FeCy_6FeK or $\text{Fe}_2\text{Cy}_6\text{K}$, whilst insoluble Prussian blue, which is prepared in the presence of an excess of a ferric salt, has the composition $\text{Fe}_7\text{Cy}_{18}, 13\text{H}_2\text{O}$. Turnbull's blue has formula $\text{Fe}_3\text{Cy}_{12}, 8\text{H}_2\text{O}$ or $(\text{Fe}_2\text{Cy}_6)_2\text{Fe}, 8\text{H}_2\text{O}$, and is the ferrous salt corresponding to the soluble blue. The author makes a thermometric study of these substances and the cyanide complex which they contain.

Sparteine: General Characteristics; Action of certain Reducing Agents.—Ch. Moureu and A. Valeur.—Sparteine is a liquid volatile alkaloid which has been employed in therapeutics for the past twenty years, under the form of sulphate, in the treatment of cardiac ailments. The authors investigate the physical constants of this substance, and give certain general indications as to its chemical nature. Its great stability with regard to reducing agents lead to the conclusion that the base is saturated, and that all the liaisons between the atoms are simple ones. After a single investigation of the crude formula, little doubt remains that the molecule contains two, and perhaps three, closed chains.

Isonitrosomalonic Ethers and their Transformation into Mesoxalic Ethers.—L. Bouveault and A. Wahl.—V. Meyer and A. Müller have shown synthetically that nitrosomalonic acid is in reality an isonitroso-derivative identical with the oxime of meso-oxalic acid. It follows from this that the isonitrosomalonic ethers, $\text{NOH} = \text{C} \begin{smallmatrix} \text{CO}_2\text{R} \\ \text{CO}_2\text{R} \end{smallmatrix}$, constitute the oximes of the corresponding meso-oxalates, $\text{CO} \begin{smallmatrix} \text{CO}_2\text{R} \\ \text{CO}_2\text{R} \end{smallmatrix}$. These latter bodies being difficult of preparation, the authors obtain them by saponification of their oximes and investigate their properties.

Action of Ammonia on Ethylene Oxide of β -o-Cyclohexanediol.—Léon Brunel.—In a previous paper the author describes the preparation of certain addition products of ethylene oxide of β -o-cyclohexanediol. He now investigates the compounds obtained by the action of NH_3 on this ether, and obtains the following compounds:—Orthoaminocyclohexanol, $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{NH}_2$; and, by reducing the proportion of ammonia, obtains two isomeric dioxycyclohexylamines, $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{NH} \cdot \text{C}_6\text{H}_{10} \cdot \text{OH}$.

No. 4, July 27, 1903.

Preparation and Properties of Ruthenium Silicide.—Henri Moissan and Wilhem Manchot.—At the temperature of fusion of ruthenium this metal easily combines with silicon to give a silicide of formula RuSi , of density 5.40, perfectly crystalline, of great hardness, and very stable in presence of a large number of reagents.

Arsenic in Sea-water, Table Salt, Mineral Waters, &c.; its Estimation in certain ordinary Reagents.—Armand Gautier.—It has been known for some time that sea-water contains a small proportion of arsenic. The author estimates, by his method described in a recent paper, the arsenic in the water 30 km. from the coast of Brittany under the three forms—mineral, organic, and organised. Similar estimations are made on the arsenic in mineral waters and in the principal reagents used for the detection of this substance in physiology.

A Combination of two Bodies which on raising the Temperature Unite, and which Separate below -79° .—D. Grenz.—Acetone forms with mercuric iodide a solid orange-yellow combination, which is produced by the elevation of temperature a little above -94.9° , but which is only stable up to the temperature of -79° , at which temperature it is completely destroyed.

Simultaneous Separation and Estimation of Baryta, Strontia, and Lime.—Lucien Robin.—The author describes a simple method for the separation and estimation of the three metals of the alkaline earths simultaneously when present in acid solution. The liquid is first rendered alkaline by ammonia, acidified with acetic acid, boiled, and potassium bichromate added in excess. The baryta is separated as chromate. The strontia is next separated by rendering the filtrate ammoniacal, boiling it, and introducing pure ammonium sulphate. The strontia is weighed as sulphate.

Condensation of Acetylenic Ethers with Alcohol.—Ch. Moureu.—Methyl phenylpropionate, under the action of sodium methylate, can fix 2 or 1 mols. of methylic alcohol by the total or partial saturation of the acetylenic function. The new compounds thus formed correspond to benzoylacetic and cinnamic acids. The yield is usually about four-fifths of the theoretical yield.

Constitution of Allyl Cyanide.—R. Lespiau.—Allyl cyanide is prepared by the action of potassium cyanide in the cold on allyl bromide, and as a result of the author's researches on this substance he believes it to correspond to the formula $\text{CH}_2=\text{CH}-\text{CH}_2\text{CN}$.

Quinone-diketones.—Æchser de Coninck.—The author's researches lead him to believe that the molecule of the quinone-diketones, quinone-phenols, &c., at a given temperature, and under the influence of H_2SO_4 , rupture between the group CO and the substituted or non-substituted benzenic group. Afterwards these latter groups are decomposed and act on sulphuric acid, which is energetically reduced. By this means the rapid and abundant evolution of SO_2 , which the author observes in all his experiments, is explained. Alizarine and purpurine are less resisting than anthraquinone.

Albumenoid matter in Maize Seed.—MM. Donard and Labbé.—The authors continue their research on the special properties of maiseine, the albumenoid matter extracted from maize by means of boiling amylic alcohol.

MISCELLANEOUS.

Appointment.—Messrs. Howards and Sons inform us that they have entrusted to Mr. Edward White, B.Sc., F.I.C., the management of that branch of their business dealing with the manufacture of fine chemicals, and carried on under the style of Messrs. Hopkin and Williams, at Cross Street, Hatton Garden, E.C., which until recently was under the management of the late H. C. Everson, F.I.C. Messrs. Hopkin and Williams have a newly-built and equipped factory at Ilford, where the laboratories afford ample scope for research work in chemical technology and extension of business under Mr. White's direction. Mr. White, who is a Bachelor of Science of London University, and a Fellow of the Institute of Chemistry, was formerly Bell Scholar in the Pharmaceutical Society's School, acting afterwards as Demonstrator in the chemical laboratories at Bloomsbury Square. For the last fourteen years he has been in charge of the Pharmaceutical Department at St. Thomas's Hospital, where he has carried out original work dealing with pharmaceutical chemistry, one of the latest contributions from his laboratory being the solution of the time-honoured kino gelatinisation problem. Mr. White is also well known as joint-author of "Pharmacopœdia," and as the compiler of the last edition of the "St. Thomas's Hospital Pharmacopœia." At the recent

Bristol meeting of the British Pharmaceutical Conference he was appointed one of the Honorary General Secretaries to fill the vacancy caused by the retirement of Mr. F. Ransom.

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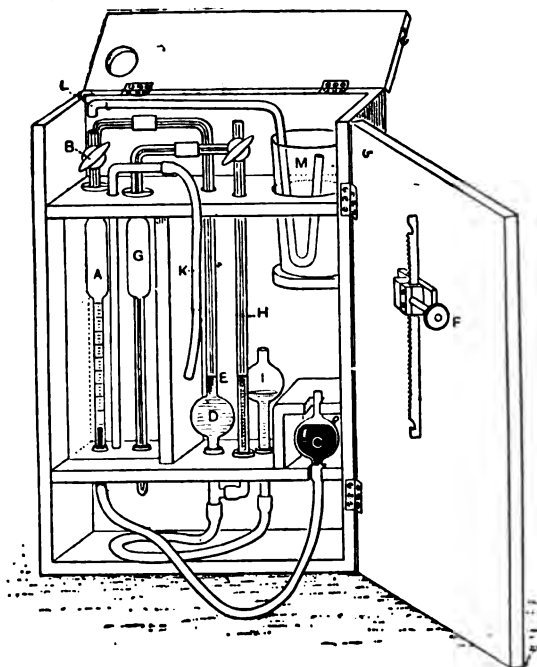
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Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Lecturer—Herbert Jackson, F.C.S.

Demonstrators—P. H. Kirkaldy, F.C.S., and D. Northall Laurie, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1903-1904 are October 1, January 13, and April 20.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visà voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, LL.D., F.R.S., &c. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—Morris Travers, D.Sc.; E. C. C. Baly, F.I.C.; N. T. M. Wilmshire, M.Sc.; and S. Smiles, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October to December; Second Term, from January to March; Third Term, from April to June. Class Examinations begin in June.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; for the First or Second Terms, £4 4s.

In this Course the physical principles bearing on Chemistry, are first discussed, and the Chemistry of the Elements and their compounds are treated in considerable detail, under the headings—Elements; halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

An Exercise Class will meet once a week throughout the Session.

Senior Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification,

the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent researches bearing on Chemical Theory.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Organic Chemistry.

Mondays, Wednesdays, and Fridays, at 9, during the session.

This Course will consist of three lectures a week during the whole Session, and is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week during the First, Second, and third Terms, for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and H. Burrows, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship

of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from 2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-second Session will commence on Oct. 1, 1903.

Professors.—Chemistry, W. Palmer Wynne, D.Sc., F.R.S., F.I.C. Sec. C.S.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—E. J. Wilkinson.

The College is open to male and female students above the age of sixteen years. The Session commences on Sept. 28th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1903-1904, Course B). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Pros-

peaches issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc. Scholar Assistant, C. K. Tinkler.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 1st, 1903. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of about 60 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term;

twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, D.Sc., Ph.D.

Demonstrator—Oliver C. M. Davis, B.Sc.

The session 1903-1904 will begin on October 6. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar and Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Elementary and Intermediate Courses.

Advanced Course (Parts I. and II.).—One Lecture a week

in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

Pharmaceuticals.—During the first and second Terms a course of Lectures will be given one evening a week dealing chiefly with the Materia Medica, Pharmacy, and Chemistry of the British Pharmacopœia. Fee, £1 1s.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar and Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell-Smith, B.Sc., F.I.C., F.C.S.; H. A. M. Borland, A.R.C.S.; A. J. Carrier, B.Sc.

Demonstrators—E. H. T. Parker; H. C. Shilstone; H. R. Tutton.

Assistant in Chemical Laboratory—C. E. Young.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 28th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.

Assistant Lecturers and Demonstrators—Alex. McKenzie, M.A., D.Sc., Ph.D.; Alex. Findlay, M.A., D.Sc., Ph.D.

The Session will be opened on October 5th, 1903.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—**Advanced Organic Chemistry.**—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. **General and Physical Chemistry.**—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General, Physical, and Organic Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.); S. F. Stell, F.C.S.; and W. Trotter.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—W. J. Willis.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. **General Chemistry Course**, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. **Chemistry and Dyeing**, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. **Chemical Engineering**. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. **Sanitary Science**. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. **Dyeing**. Extending over one or two years.

VI. **Textile and Dyeing**. Arranged for those Students who desire to study the two subjects simultaneously.

VII. **First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)**, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. **General Pharmaceutical Course**. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

IX. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

**ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER.**

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemo-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

**VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.**

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D.

Assistant Lecturers and Demonstrators—T. S. Patterson, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrators—C. E. Whiteley, M.Sc., and W. Lowson, B.Sc., A.I.C.

The Session begins October, 1903.

Lecture Courses.

1. **General Course of Chemistry**.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. **Advanced Inorganic Chemistry**.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. **Advanced Inorganic Chemistry**.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. **Organic Chemistry**.—Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—

(a) **Organic Chemistry**.—Monday, Wednesday, and Friday at 12 noon in the First and Second Terms. Fee, £2 12s. 6d.

(b) **History of Chemistry**.—Monday, Wednesday, and Friday at 9.30 a.m. in the First Term. Fee, £1 11s. 6d.

(c) **Physical Chemistry**.—Tuesday, Thursday, and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 12s. 6d.

(d) **Electro-chemistry**.—One hour weekly. 31s. 6d.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m.

to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s. *Practical Course in Sanitary Chemistry*.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

Assistant Lecturer and Demonstrator of Practical Dyeing—Percival J. Wood.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the Yorkshire College.

UNIVERSITY OF LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—A. T. de Moulipied, B.Sc., Ph.D.; and A. W. Titherley, D.Sc., Ph.D.; F. J. Brislee, B.Sc.

Assistant—H. H. Froydell.

The Session commences October 1st.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of the University; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes

qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry, with Practical Work. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Preliminary. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories recently enlarged provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, and a Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the University Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course D or E, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the B.Sc. Degree of the University of Liverpool, or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1903, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1903. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Secretary, University of Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—J. A. Smythe, M.Sc., Ph.D., and H. W. Cousins, B.Sc.

First Year Courses.—1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

11. *Special Course.*—More advanced than the above. Mondays and Fridays, 11 to 12. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 6th.

The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s. Also special class in Crystallography.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the second year in an examination in a more advanced stage in any two of these subjects. Associates in Science are admissible one year after obtaining the title of Associate to the examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 28th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 28th. Candidates should send in their names to the Secretary on or before September 21st.

**OWENS COLLEGE,
THE VICTORIA UNIVERSITY OF MANCHESTER.**

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; F. V. Darbishire, B.A., Ph.D.

Demonstrator in Organic Chemistry—D. T. Jones, B.Sc.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Lecturer in Metallurgy—Dr. Bone.

Lecturer in Electro-Chemistry—R. S. Hutton, B.Sc.

The Session begins on October 6, 1903.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

CHEMICAL LABORATORIES.—These are again being extended. Two large rooms will be added to the main laboratories; one for Inorganic and one for Organic work. These will connect the present buildings to the Schunck Laboratory. The Laboratory and Chemical Library belonging to the late Dr. E. Schunck, F.R.S., left by him in 1902 for the use of the Owens College, is being erected in Burlington Street. The Schunck Laboratory is to be devoted to research work.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

METALLURGY.—*Lectures:* (A) The Metallurgy of Copper, Lead, Silver, Gold, Zinc, and Antimony; and (B) the Metallurgy of Iron and Steel.

The Metallurgical Laboratory, which is open every day in the week, has recently been re-equipped with a view to research work on the structure and properties of Steel and other Alloys, and the Chemistry of Fuel and Gases.

ELECTRO-CHEMISTRY.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. There is a complete equipment for Electro-chemical and Electro-metallurgical work. Demonstrator and Assistant Lecturer in Electro-technics, Robert Beattie, B.Sc. (Durham). Demonstrator and Assistant Lecturer in Electro-chemistry, R. S. Hutton, M.Sc. (Vi&.).

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—
First year: First year Honours Lectures; Mathematics

(3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry or Metallurgy Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £100 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; &c.

Schunck Fellowship.—A Fellowship for Chemical Research will be offered during the Session 1903-4 under the Schunck endowment, a portion of the income arising from which is at present used for providing expensive material required in research work. Students may be appointed to Research Studentships, which entitle the holders to work in the laboratories under reduced fees.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. D. Lander, D.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 5th, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on Electrochemistry and other special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Pharmacy, Materia Medica, and all other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 1st.

Matriculation Course.—Tuesday and Friday 10 to 11. Fee, £2 12s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 1s. Honours: Tuesdays and Thursdays, 12

to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9. Sessional Fee, Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works is now being erected in connection with the Sheffield College at a cost of about £10,000. The works are designed to include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works will also be provided with a hammer and rolling mill capable of dealing with four-inch ingots. Differential annealing furnaces, oil-brightening and lead-tempering tanks will constitute part

of the new plant. Additional laboratory accommodation will be attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 7th, and ends on March 6th. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—A. N. Meldrum, B.Sc., and F. W. Gray, M.A., B.Sc.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. Special Lecture Course on Organic Chemistry (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

III. Practical Course for Medical Students.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. Chemical Laboratory.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. Physical and Advanced Inorganic Chemistry (30 Lectures).—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. A. N. Meldrum. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated

of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Phy-

siology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.
Professor—John Gibson, Ph.D., F.R.S.E.
Assisted by the following Lecturers and Demonstrators:—Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and J. P. Longstaff, B.Sc.

The Session begins September 28th, 1903.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the third year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £12 12s.; for Chemistry Courses, £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and

passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1903-1904 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for fifty-one Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 25th and following days. Thirty-three of these Bursaries are restricted to Men, four to Men or Women, and fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Second B.Sc. Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for each course of Practical Chemistry is £3 3s.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—Laboratory Pupils.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session will commence on October 20th, 1903, and end on June 11th, 1904. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1903.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a

Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which Chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time also been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Thomas Walsh, B.A.

Research Assistants—W. Sloan Mills, M.A., and Francis M. G. Micklethwait, A.R.C.S.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the third time to a Chemistry Student of this College, and to another Student it has been renewed for a third year.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Lecturer on Organic Chemistry—F. G. Donnan, M.A., Ph.D.

Assistant Chemist—J. Holmes Pollok, B.Sc.

Demonstrator of Chemistry and Assaying—A. E. B. Manders.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering

and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitors, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateship Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing

works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 22nd, and the Winter Session opens on Tuesday, October 6th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 22nd. Session begins October 6th. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, B.Sc., &c. Session commences Sept. 28.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. inorganic, Organic, and Technological Chemistry. Mr. John Wilson, M.Sc. (Vit.), assisted by John L. White, M.Sc., H. G. Wayling, B.Sc., Mr. H. Evans, Mr. A. Rowan, and others. Session opens Sept. 21. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper Testing, Paper Making, Gas Manufacture, Gas Analysis, Oils, Fats, and Soaps, Chemistry of Building Materials, Chemistry of Foods, &c.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. J. E. Mackenzie prepares for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty years of educational work in the metropolis, commences its new Session on Monday, September 28th, when an opening address will be delivered by Dr. Emil Reich. The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, Classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, and also for those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 67 students passed some university examination, while large numbers gained successes at other public examinations. The College has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. The Day classes provide courses in Chemistry, Biology, Botany, Physics, Mathematics, and Geology for the Science Degrees of London University, and a complete course of instruction in Metallurgy and Mining. There are also Day classes in Latin, Greek, and modern Languages, including Russian and Spanish. The School of Art is open both day and evening. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes

and full information about the College. A Lecture or Entertainment is given in the Theatre every Wednesday evening.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S.(Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings (70s.). Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by A. Fontana, B.A. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 10s.). Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 28, 1903.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, &c. Systematic Courses are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 34d.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Arthur Lapworth, D.Sc.(Lond.), F.I.C.; Assistants, Mr. A. C. O. Hann and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 21.

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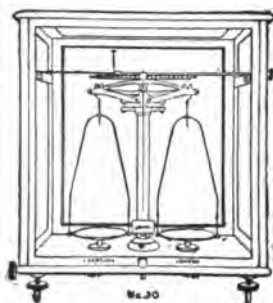
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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTHPORT, 1903.

INAUGURAL ADDRESS OF THE PRESIDENT,

SIR NORMAN LOCKYER, K.C.B., LL.D., F.R.S.,
Correspondant de l'Institut de France.

The Influence of Brain-power on History.

My first duty to-night is a sad one. I have to refer to a great loss which this nation and this Association have sustained. By the death of the great Englishman and great statesman who has just passed away we members of the British Association are deprived of one of the most illustrious of our Past-Presidents. We have to mourn the loss of an enthusiastic student of science. We recognise that as Prime Minister he was mindful of the interests of science, and that to him we owe a more general recognition on the part of the State of the value to the nation of the work of scientific men. On all these grounds you will join in the expression of respectful sympathy with Lord Salisbury's family in their great personal loss which your Council has embodied this morning in a resolution of condolence.

Last year, when this friend of science ceased to be Prime Minister, he was succeeded by another statesman who also has given many proofs of his devotion to philosophical studies, and has shown in many utterances that he has a clear understanding of the real place of science in modern civilisation. We, then, have good grounds for hoping that the improvement in the position of science in this country which we owe to the one will also be the care of his successor, who has honoured the Association by accepting the unanimous nomination of your Council to be your President next year, an acceptance which adds a new lustre to this Chair.

On this we may congratulate ourselves all the more because I think, although it is not generally recognised, that the century into which we have now well entered may be more momentous than any which has preceded it, and that the present history of the world is being so largely moulded by the influence of brain-power, which in these modern days has to do with natural as well as human forces and laws, that statesmen and politicians will have in the future to pay more regard to education and science as empire-builders and empire-guardians than they have paid in the past.

The nineteenth century will ever be known as the one in which the influences of science were first fully realised in civilised communities; the scientific progress was so gigantic that it seems rash to predict that any of its successors can be more important in the life of any nation.

Disraeli, in 1873, referring to the progress up to that year, spoke as follows:—"How much has happened in these fifty years—a period more remarkable than any, I will venture to say, in the annals of mankind. I am not thinking of the rise and fall of Empires, the change of dynasties, the establishment of Governments. I am thinking of those revolutions of science which have had much more effect than any political causes, which have changed the position and prospects of mankind more than all the conquests and all the codes and all the legislators that ever lived" (*Nature*, November 27, 1873, vol. ix., p. 71).

The progress of science, indeed, brings in many considerations which are momentous in relation to the life of

any limited community—any one nation. One of these considerations to which attention is now being greatly drawn is that a relative decline in national wealth derived from industries must follow a relative neglect of scientific education.

It was the late Prince Consort who first emphasised this when he came here fresh from the University of Bonn. Hence the "Prince Consort's Committee," which led to the foundation of the College of Chemistry, and afterwards of the Science and Art Department. From that time to this the warnings of our men of science have become louder and more urgent in each succeeding year. But this is not all; the commercial output of one country in one century as compared with another is not alone in question; the acquirement of the scientific spirit and a knowledge and utilisation of the forces of Nature are very much further reaching in their effects on the progress and decline of nations than is generally imagined.

Britain in the middle of the last century was certainly the country which gained most by the advent of science, for she was then in full possession of those material gifts of Nature, coal and iron, the combined winning and utilisation of which, in the production of machinery and in other ways, soon made her the richest country in the world, the seat and throne of invention and manufacture, as Mr. Carnegie has called her. Being the great producers and exporters of all kinds of manufactured goods, we became eventually, with our iron ships, the great carriers, and hence the supremacy of our mercantile marine and our present command of the sea.

The most fundamental change wrought by the early applications of science was in relation to producing and carrying power. With the winning of mineral wealth and the production of machinery in other countries, and cheap and rapid transit between nations, our superiority as depending upon our first use of vast material resources was reduced. Science, which is above all things cosmopolitan—planetary, not national—internationalises such resources at once. In every market of the world

"things of beauty, things of use,
Which one fair planet can produce,
Brought from under every star,"

were soon to be found.

Hence the first great effect of the general progress of science was relatively to diminish the initial supremacy of Britain due to the first use of material resources, which indeed was the real source of our national wealth and place among the nations.

The unfortunate thing was that, while the foundations of our superiority depending upon our material resources were being thus sapped by a cause which was beyond our control, our statesmen and our Universities were blind leaders of the blind, and our other asset, our mental resources, which was within our control, was culpably neglected.

So little did the bulk of our statesmen know of the part science was playing in the modern world and of the real basis of the nation's activities that they imagined political and fiscal problems to be the only matters of importance. Nor, indeed, are we very much better off to-day. In the important discussions recently raised by Mr. Chamberlain next to nothing has been said of the effect of the progress of science on prices. The whole course of the modern world is attributed to the presence or absence of taxes on certain commodities in certain countries. The fact that the great fall in the price of food-stuffs in England did not come till some thirty or forty years after the removal of the corn duty between 1847 and 1849 gives them no pause; for them new inventions, railways, and steamships are negligible quantities; the vast increase in the world's wealth, in Free Trade and Protected countries alike, comes merely, according to them, in response to some political shibboleth.

We now know, from what has occurred in other States, that if our Ministers had been more wise and our Universities more numerous and efficient our mental resources would have been developed by improvements in educational

method, by the introduction of science into schools, and, more important than all the rest, by the teaching of science by experiment, observation, and research, and not from books. It is because this was not done that we have fallen behind other nations in properly applying science to industry, so that our applications of science to industry are relatively less important than they were. But this is by no means all; we have lacked the strengthening of the national life produced by fostering the scientific spirit among all classes and along all lines of the nation's activity; many of the responsible authorities know little and care less about science; we have not learned that it is the duty of a State to organise its forces as carefully for peace as for war; that Universities and other teaching centres are as important as battleships or big battalions; are, in fact, essential parts of a modern State's machinery, and, as such, to be equally aided and as efficiently organised to secure its future well-being.

Now the objects of the British Association as laid down by its founders seventy-two years ago are "To give a stronger impulse and a more systematic direction to scientific inquiry—to promote the intercourse of those who cultivate science in different parts of the British Empire with one another, and with foreign philosophers—to obtain a more general attention to the objects of science and a removal of any disadvantages of a public kind which impede its progress."

In the main, my predecessors in this Chair, to which you have done me the honour to call me, have dealt, and with great benefit to science, with the objects first named.

But at a critical time like the present I find it imperative to depart from the course so generally followed by my predecessors and to deal with the last object named, for unless by some means or other we "obtain a more general attention to the objects of science, and a removal of any disadvantages of a public kind which impede its progress," we shall suffer in competition with other communities in which science is more generally utilised for the purposes of the national life.

The Struggle for Existence in Modern Communities.

Some years ago, in discussing the relations of scientific instruction to our industries, Huxley pointed out that we were in presence of a new "struggle for existence," a struggle which, once commenced, must go on until only the fittest survives.

It is a struggle between organised species—nations—not between individuals or any class of individuals. It is, moreover, a struggle in which science and brains take the place of swords and sinews, on which depended the result of those conflicts which, up to the present, have determined the history and fate of nations. The school, the University, the laboratory, and the workshop are the battlefields of this new warfare.

But it is evident that if this, or anything like it, be true, our industries cannot be involved alone; the scientific spirit, brain-power, must not be limited to the workshop, if other nations utilise it in all branches of their administration and executive.

It is a question of an important change of front. It is a question of finding a new basis of stability for the Empire in face of new conditions. I am certain that those familiar with the present state of things will acknowledge that the Prince of Wales's call, "Wake up," applies quite as much to the members of the Government as it does to the leaders of industry.

What is wanted is a complete organisation of the resources of the nation, so as to enable it best to face all the new problems which the progress of science, combined with the ebb and flow of population and other factors in international competition, are ever bringing before us. Every Minister, every public department, is involved; and this being so, it is the duty of the whole nation—King, Lords, and Commons—to do what is necessary to place our scientific institutions on a proper footing in order to

enable us to "face the music," whatever the future may bring. The idea that science is useful only to our industries comes from want of thought. If anyone is under the impression that Britain is only suffering at present from the want of the scientific spirit among our industrial classes, and that those employed in the State service possess adequate brain-power and grip of the conditions of the modern world into which science so largely enters, let him read the Report of the Royal Commission on the War in South Africa. There he will see how the whole "system" employed was, in Sir Henry Brackenbury's words applied to a part of it, "*unsuited to the requirements of an army which is maintained to enable us to make war.*" Let him read also in the Address of the President of the Society of Chemical Industry what drastic steps had to be taken by Chambers of Commerce and "a quarter of a million of working-men" to get the Patent Law Amendment Act into proper shape in spite of all the advisers and officials of the Board of Trade. Very few people realise the immense number of scientific problems the solution of which is required for the State service. The nation itself is a gigantic workshop; and the more our rulers and legislators, administrators, and executive officers possess the scientific spirit, the more the rule-of-thumb is replaced in the State service by scientific methods, the more able shall we be, thus armed at all points, to compete successfully with other countries along all lines of national as well as of commercial activity.

It is obvious that the power of a nation for war, in men and arms and ships, is one thing; its power in the peace struggles to which I have referred is another. In the latter the source and standard of national efficiency are entirely changed. To meet war conditions, there must be equality or superiority in battleships and army corps. To meet the new peace conditions, there must be equality or superiority in Universities, scientific organisation, and everything which conduces to greater brain-power.

Our Industries are suffering in the present International Competition.

The present condition of the nation, so far as its industries are concerned, is as well known, not only to the Prime Minister, but to other political leaders in and out of the Cabinet, as it is to you and to me. Let me refer to two speeches delivered by Lord Rosebery and Mr. Chamberlain on two successive days in January, 1901.

Lord Rosebery spoke as follows:—

"... The war I regard with apprehension is the war of trade which is unmistakably upon us. . . . When I look round me I cannot blind my eyes to the fact that, so far as we can predict anything of the twentieth century on which we have now entered, it is that it will be one of acutest international conflict in point of trade. We were the first nation of the modern world to discover that trade was an absolute necessity. For that we were nicknamed a nation of shopkeepers; but now every nation wishes to be a nation of shopkeepers too, and I am bound to say that when we look at the character of some of these nations, and when we look at the intelligence of their preparations, we may well feel that it behoves us not to fear, but to gird up our loins in preparation for what is before us."

Mr. Chamberlain's views were stated in the following words:—

"I do not think it is necessary for me to say anything as to the urgency and necessity of scientific training. . . . It is not too much to say that the existence of this country, as the great commercial nation, depends upon it. . . . It depends very much upon what we are doing now, at the beginning of the twentieth century, whether at its end we shall continue to maintain our supremacy or even equality with our great commercial and manufacturing rivals."

All this refers to our industries. We are suffering because trade no longer follows the flag as in the old days, but because trade follows the brains, and our manufacturers

are too apt to be careless in securing them. In one chemical establishment in Germany 400 doctors of science, the best the Universities there can turn out, have been employed at different times in late years. In the United States the most successful students in the higher teaching centres are snapped up the moment they have finished their course of training, and put into charge of large concerns, so that the idea has got abroad that youth is the password of success in American industry. It has been forgotten that the latest product of the highest scientific education must necessarily be young, and that it is the training and not the age which determines his employment. In Britain, on the other hand, apprentices who can pay high premiums are too often preferred to those who are well educated, and the old rule-of-thumb processes are preferred to new developments—a conservatism too often depending upon the master's own want of knowledge.

I should not be doing my duty if I did not point out that the defeat of our industries one after another, concerning which both Lord Rosebery and Mr. Chamberlain express their anxiety, is by no means the only thing we have to consider. The matter is not one which concerns our industrial classes only, for knowledge must be pursued for its own sake; and since the full life of a nation with a constantly increasing complexity, not only of industrial, but of high national aims, depends upon the universal presence of the scientific spirit—in other words, brain-power—our whole national life is involved.

The Necessity for a Body dealing with the Organisation of Science.

The present awakening in relation to the nation's real needs is largely due to the warnings of men of science. But Mr. Balfour's terrible Manchester picture of our present educational condition* shows that the warning, which has been going on now for more than fifty years, has not been forcible enough; but if my contention that other reorganisations besides that of our education are needed is well founded, and if men of science are to act the part of good citizens in taking their share in endeavouring to bring about a better state of things, the question arises: Has the neglect of their warnings so far been due to the way in which these have been given?

Lord Rosebery, in the address to a Chamber of Commerce from which I have already quoted, expressed his opinion that such bodies do not exercise so much influence as might be expected of them. But if commercial men do not use all the power their organisation provides, do they not by having built up such an organisation put us students of science to shame, who are still the most disorganised members of the community?

Here, in my opinion, we have the real reason why the scientific needs of the nation fail to command the attention either of the public or of successive Governments. At present, appeals on this or on that behalf are the appeals of individuals; science has no collective voice on the larger national questions; there is no organised body which formulates her demands.

During many years it has been part of my duty to consider such matters, and I have been driven to the conclusion that our great crying need is to bring about an organisation of men of science and all interested in science similar to those which prove so effective in other branches of human activity. For the last few years I have dreamt of a Chamber, Guild, League, call it what you will, with a wide and large membership, which should give us what, in my opinion, is so urgently needed. Quite recently I sketched out such an organisation, but what was my astonishment to find that I had been forestalled, and by the founders of the British Association!

The British Association such a Body.

At the commencement of this Address, I pointed out that one of the objects of the Association, as stated by its founders, was "to obtain a more general attention to the objects of science and a removal of any disadvantages of a public kind which impede its progress."

Everyone connected with the British Association from its beginning may be congratulated upon the magnificent way in which the other objects of the Association have been carried out; but as one familiar with the Association for the last forty years, I cannot but think that the object to which I have specially referred has been too much overshadowed by the work done in connection with the others.

A careful study of the early history of the Association leads me to the belief that the function I am now dwelling on was strongly in the minds of the founders; but be this as it may, let me point out how admirably the organisation is framed to enable men of science to influence public opinion, and so to bring pressure to bear upon Governments which follow public opinion. (1) Unlike all the other chief metropolitan societies, its outlook is not limited to any branch or branches of science. (2) We have a wide and numerous fellowship, including both the leaders and the lovers of science, in which all branches of science are and always have been included with the utmost catholicity—a condition which renders strong committees possible on any subject. (3) An annual meeting at a time when people can pay attention to the deliberations, and when the newspapers can print reports. (4) The possibility of beating up recruits, and establishing local committees in different localities, even in the King's dominions beyond the seas, since the place of meeting changes from year to year, and is not limited to these islands.

We not only, then, have a scientific Parliament competent to deal with all matters, including those of national importance, relating to science, but machinery for influencing all new councils and committees dealing with local matters, the functions of which are daily becoming more important.

The machinery might consist of our corresponding societies. We already have affiliated to us seventy societies with a membership of 25,000. Were this number increased so as to include every scientific society in the Empire, metropolitan and provincial, we might eventually hope for a membership of half a million.

I am glad to know that the Council is fully alive to the importance of giving a greater impetus to the work of the corresponding societies. During this year a committee was appointed to deal with the question: and later still, after this committee had reported, a conference was held between this committee and the corresponding societies committee to consider the suggestions made, some of which will be gathered from the following extract:—

"In view of the increasing importance of science to the nation at large, your committee desire to call the attention of the Council to the fact that in the corresponding societies the British Association has gathered in the various centres represented by these societies practically all the scientific activity of the provinces. The number of members and associates at present on the list of the corresponding societies approaches 25,000, and no organisation is in existence anywhere in the country better adapted than the British Association for stimulating, encouraging, and co-ordinating all the work being carried on by the seventy societies at present enrolled. Your committee are of opinion that further encouragement should be given to these societies and their individual working members by every means within the power of the Association; and with the object of keeping the corresponding societies in more permanent touch with the Association they suggest that an official invitation on behalf of the Council be addressed to the societies, through the corresponding societies committee, asking them to appoint standing British Association sub-committees, to be elected by themselves, with the object of dealing with all those subjects of investigation common to their societies and to

* "The existing educational system of this country is chaotic, is ineffectual, is utterly behind the age, makes us the laughing-stock of every advanced nation in Europe and America, puts us behind, not only our American cousins, but the German and the Frenchman and the Italian."—*Times*, October 15, 1902.

the British Association committees, and to look after the general interests of science and scientific education throughout the provinces and provincial centres.

"Your committee desire to lay special emphasis on the necessity for the extension of the scientific activity of the corresponding societies and the expert knowledge of many of their members in the direction of scientific education. They are of opinion that immense benefit would accrue to the country if the corresponding societies would keep this requirement especially in view with the object of securing adequate representation for scientific education on the Education Committees now being appointed under the new Act. The educational section of the Association having been but recently added, the corresponding societies have as yet not had much opportunity for taking part in this branch of the Association's work; and in view of the re-organisation in education now going on all over the country, your committee are of opinion that no more opportune time is likely to occur for the influence of scientific organisations to make itself felt as a real factor in national education. . . ."

I believe that if these suggestions or anything like them—for some better way may be found on inquiry—are accepted, great good to science throughout the Empire will come. Rest assured that sooner or later such a Guild will be formed because it is needed. It is for you to say whether it shall be, or form part of, the British Association. We in this Empire certainly need to organise science as much as in Germany they find the need to organise a navy. The German Navy League, which has branches even in our Colonies, already has a membership of 630,000, and its income is nearly £20,000 a year. A British Science League of 500,000 with a sixpenny subscription would give us £12,000 a year, quite enough to begin with.

I for one believe that the British Association would be a vast gainer by such an expansion of one of its existing functions. Increased authority and prestige would follow its increased utility. The meetings would possess a new interest; there would be new subjects for reports; missionary work less needed than formerly would be replaced by efforts much more suited to the real wants of the time. This magnificent, strong, and complicated organisation would become a living force, working throughout the year instead of practically lying idle, useless, and rusting for fifty-one weeks out of the fifty-two so far as its close association with its members is concerned.

If this suggestion in any way commends itself to you, then when you begin your work in your sections or General Committee see to it that a body is appointed to inquire how the thing can be done. Remember that the British Association will be as much weakened by the creation of a new body to do the work I have shown to have been in the minds of its founders as I believe it will be strengthened by becoming completely effective in every one of the directions they indicated, and for which effectiveness we, their successors, are indeed responsible. The time is appropriate for such a reinforcement of one of the wings of our organisation, for we have recently included Education among our sections.

There is another matter I should like to see referred to the committee I have spoken of, if it please you to appoint it. The British Association—which, as I have already pointed out, is now the chief body in the Empire which deals with the totality of science—is, I believe, the only organisation of any consequence which is without a charter, and which has not his Majesty the King as patron.

The First Work of such an Organisation.

I suppose it is my duty, after I have suggested the need of organisation, to tell you my personal opinion as to the matters where we suffer most in consequence of our lack of organisation at the present time.

Our position as a nation, our success as merchants, are in peril chiefly—dealing with preventable causes—because of our lack of completely efficient Universities and our neglect of research. This research has a double end. A

professor who is not learning cannot teach properly or arouse enthusiasm in his students; while a student of anything who is unfamiliar with research methods, and without that training which research brings, will not be in the best position to apply his knowledge in after-life. From neglect of research comes imperfect education, and a small output of new applications and new knowledge to re-invigorate our industries. From imperfect education comes the un-concern touching scientific matters, and the too frequent absence of the scientific spirit in the nation generally, from the Court to the Parish Council.

I propose to deal as briefly as I can with each of these points.

Universities.

I have shown that, so far as our industries are concerned, the cause of our failure has been run to earth; it is fully recognised that it arises from the insufficiency of our Universities both in numbers and efficiency, so that not only our captains of industry, but those employed in the nation's work generally, do not secure a training similar to that afforded by other nations. No additional endowment of primary, secondary, or technical instruction will mend matters. This is not merely the opinion of men of science; our great towns know it, our Ministers know it.

It is sufficient for me to quote Mr. Chamberlain:—

"It is not everyone who can, by any possibility, go forward into the higher spheres of education; but it is from those who do that we have to look for the men who in the future will carry high the flag of this country in commercial, scientific, and economic competition with other nations. At the present moment I believe there is nothing more important than to supply the deficiencies which separate us from those with whom we are in the closest competition. In Germany, in America, in our own colony of Canada, and in Australia, the higher education of the people has more support from the Government, is carried further than it is here in the Old Country; and the result is that in every profession, in every industry, you find the places taken by men and by women who have had a University education. And I would like to see the time in this country when no man should have a chance for any occupation of the better kind, either in our factories, our workshops, or our counting-houses, who could not show proof that in the course of his University career he had deserved the position that was offered to him. What is it that makes a country? Of course you may say, and you would be quite right, 'The general qualities of the people, their resolution, their intelligence, their pertinacity, and many other good qualities.' Yes; but that is not all, and it is not the main creative feature of a great nation. The greatness of a nation is made by its greatest men. It is those we want to educate. It is to those who are able to go, it may be, from the very lowest steps in the ladder, to men who are able to devote their time to higher education, that we have to look to continue the position which we now occupy as, at all events, one of the greatest nations on the face of the earth. And, feeling as I do on these subjects, you will not be surprised if I say that I think the time is coming when Governments will give more attention to this matter, and perhaps find a little more money to forward its interests."—(*Times*, November 6, 1902).

Our conception of a University has changed. University education is no longer regarded as the luxury of the rich, which concerns only those who can afford to pay heavily for it. The Prime Minister in a recent speech, while properly pointing out that the collective effect of our public and secondary schools upon British character cannot be overrated, frankly acknowledged that the boys of seventeen or eighteen who have to be educated in them "do not care a farthing about the world they live in, except in so far as it concerns the cricket-field or the football-field or the river." On this ground they are not to be taught science; and hence, when they proceed to the University, their curriculum is limited to subjects which were better taught before the modern world existed, or even Galileo was born

But the science which these young gentlemen neglect, with the full approval of their teachers, on their way through the school and the University to politics, the Civil Service, or the management of commercial concerns, is now one of the great necessities of a nation; and our Universities must become as much the insurers of the future progress as battleships are the insurers of the present power of States. In other words, University competition between States is now as potent as competition in building battleships; and it is on this ground that our University conditions become of the highest national concern, and therefore have to be referred to here, and all the more because our industries are not alone in question.

Why we have not more Universities.

Chief among the causes which have brought us to the terrible condition of inferiority as compared with other nations in which we find ourselves, are our carelessness in the matter of education, and our false notions of the limitations of State functions in relation to the conditions of modern civilisation.

Time was when the Navy was largely a matter of private and local effort. William the Conqueror gave privileges to the Cinque Ports on the condition that they furnished fifty-two ships when wanted. In the time of Edward III., of 730 sail engaged in the siege of Calais, 705 were "people's ships." All this has passed away; for our first line of defence we no longer depend on private and local effort.

Time was when not a penny was spent by the State on elementary education. Again, we no longer depend upon private and local effort. The Navy and primary education are now recognised as properly calling upon the public for the necessary financial support. But when we pass from primary to University education, instead of State endowment we find State neglect; we are in a region where it is nobody's business to see that anything is done.

We in Great Britain have thirteen Universities competing with 134 State and privately endowed in the United States, and twenty-two State endowed in Germany. I leave other countries out of consideration for lack of time, and I omit all reference to higher institutions for technical training, of which Germany alone possesses nine of University rank, because they are less important; they instruct rather than educate, and our want is education. The German State gives to one University more than the British Government allows to all the Universities and University Colleges in England, Ireland, Scotland, and Wales put together. These are the conditions which regulate the production of brain-power in the United States, Germany, and Britain respectively, and the excuse of the Government is that this is a matter for private effort. Do not our Ministers of State know that other civilised countries grant efficient State aid, and, further, that private effort has provided in Great Britain less than 10 per cent of the sum thus furnished in the United States in addition to State aid? Are they content that we should go under in the great struggle of the modern world because the Ministers of other States are wiser, and because the individual citizens of another country are more generous than our own?

If we grant that there was some excuse for the State's neglect so long as the higher teaching dealt only with words, and books alone had to be provided (for the streets of London and Paris have been used as class-rooms at a pinch), it must not be forgotten that during the last hundred years not only has knowledge been enormously increased, but things have replaced words, and fully equipped laboratories must take the place of books and class-rooms if University training worthy of the name is to be provided. There is much more difference in size and kind between an old and a new University than there is between the old caravel and a modern battleship, and the endowments must follow suit.

What are the facts relating to private endowment in this country? In spite of the munificence displayed by a small number of individuals in some localities, the truth must be

spoken. In depending in our country upon this form of endowment we are trusting to a broken reed. If we take the twelve English University Colleges, the forerunners of Universities unless we are to perish from lack of knowledge, we find that private effort during sixty years has found less than £4,000,000; that is, £2,000,000 for buildings and £40,000 a year income. This gives us an average of £166,000 for buildings and £3300 for yearly income.

What is the scale of private effort we have to compete with in regard to the American Universities?

In the United States, during the last few years, Universities and colleges have received more than £40,000,000 from this source alone; private effort supplied nearly £7,000,000 in the years 1898-1900.

Next consider the amount of State aid to Universities afforded in Germany. The buildings of the new University of Strassburg have already cost nearly a million; that is, about as much as has yet been found by private effort for buildings in Manchester, Liverpool, Birmingham, Bristol, Newcastle, and Sheffield. The Government annual endowment of the same German University is more than £49,000.

This is what private endowment does for us in England, against State endowment in Germany.

But the State does really concede the principle; its present contribution to our Universities and colleges amounts to £155,600 a year. No capital sum, however, is taken for buildings. The State endowment of the University of Berlin in 1891-2 amounted to £168,777.

When, then, we consider the large endowments of University education both in the United States and Germany, it is obvious that State aid only can make any valid competition possible with either. The more we study the facts, the more statistics are gone into, the more do we find that we, to a large extent, lack both of the sources of endowment upon one or other, or both, of which other nations depend. We are between two stools, and the prospect is hopeless without some drastic changes. And first among these, it we intend to get out of the present Slough of Despond, must be the giving up of the idea of relying upon private effort.

That we lose most where the State does least is known to Mr. Chamberlain, for in his speech, to which I have referred, on the University of Birmingham, he said:—"As the importance of the aim we are pursuing becomes more and more impressed upon the minds of the people, we may find that we shall be more generously treated by the State."

Later still, on the occasion of a visit to University College School, Mr. Chamberlain spoke as follows:—

"When we are spending, as we are, many millions—I think it is £13,000,000—a year on primary education, it certainly seems as if we might add a little more, even a few tens of thousands, to what we give to University and secondary education."—(*Times*, November 6, 1902).

To compete on equal grounds with other nations we must have more Universities. But this is not all—we want a far better endowment of all the existing ones, not forgetting better opportunities for research on the part of both professors and students. Another crying need is that of more professors and better pay. Another is the reduction of fees; they should be reduced to the level existing in those countries which are competing with us—to, say, one-fifth of their present rates, so as to enable more students in the secondary and technical schools to complete their education.

In all these ways facilities would be afforded for providing the highest instruction to a much greater number of students. At present there are almost as many *professors and instructors* in the Universities and colleges of the United States as there are *day students* in the Universities and colleges of the United Kingdom.

Men of science, our leaders of industry, and the chiefs of our political parties all agree that our present want of higher education—in other words, properly equipped Universities—is heavily handicapping us in the present race for commercial supremacy, because it provides a rela-

tively inferior brain-power, which is leading to a relatively reduced national income.

The facts show that in this country we cannot depend upon private effort to put matters right. How about local effort?

Anyone who studies the statistics of modern municipalities will see that it is impossible for them to raise rates for the building and upkeep of Universities.

The buildings of the most modern Universities in Germany have cost a million. For upkeep the yearly sums found, chiefly by the State, for German Universities of different grades, taking the incomes of seven out of the twenty-two Universities as examples, are:—

First class	Berlin	£130,000
Second class ..	{ Bonn Göttingen }	.. 56,000
Third class.. ..	{ Königsberg Strassburg }	.. 48,000
Fourth class ..	{ Heidelberg Marburg }	.. 37,000

Thus, if Leeds, which is to have a University, is content with the fourth class German standard, a rate must be levied of 7d. in the pound for yearly expenses, independent of all buildings. But the facts are that our towns are already at the breaking strain. During the last fifty years, in spite of enormous increases in rateable values, the rates have gone up from about 2s. to about 7s. in the pound for real local purposes. But no University can be a merely local institution.

How to get more Universities.

What, then, is to be done? Fortunately, we have a precedent admirably in point, the consideration of which may help us to answer this question.

I have pointed out that in old days our Navy was chiefly provided by local and private effort. Fortunately for us those days have passed away; but some twenty years ago, in spite of a large expenditure, it began to be felt by those who knew, that in consequence of the increase of foreign navies our sea-power was threatened, as now, in consequence of the increase of foreign Universities, our brain-power is threatened.

The nation slowly woke up to find that its enormous commerce was no longer insured at sea, that in relation to foreign navies our own had been suffered to dwindle to such an extent that it was no longer capable of doing the duty which the nation expected of it even in times of peace. At first this revelation was received with a shrug of incredulity, and the peace-at-any-price party denied that anything was needed; but a great teacher arose;* as the facts were inquired into, the suspicion changed into an alarm; men of all parties saw that something must be done. Later, the nation was thoroughly aroused, and with an universal agreement the principle was laid down that, cost what it might to enforce our sea-power, our Navy must be made and maintained of a strength greater than those of any two possibly contending Powers. After establishing this principle, the next thing to do was to give effect to it. What did the nation do after full discussion and inquiry? A Bill was brought in in 1888, and a sum of £21,500,000 was voted in order, during the next five years, to inaugurate a large ship-building programme, so that Britain and Britain's commerce might be guarded on the high seas in any event.

Since then we have spent £120,000,000 on new ships, and this year we spend still more millions on still more new ships. If these prove insufficient to safe-guard our sea-power, there is no doubt that the nation will increase them, and I have not heard that anybody has suggested an appeal to private effort.

* Captain Mahan, of the U.S. Navy, whose book, "On the Influence of Sea-power on History," has suggested the title of my Address.

How, then, do we stand with regard to Universities, recognising them as the chief producers of brain-power and therefore the equivalents of battleships in relation to sea-power? Do their numbers come up to the standard established by the Admiralty principle to which I have referred? Let us attempt to get a rough-and-ready estimate of our educational position by counting Universities as the Admiralty counts battleships. I say rough-and-ready, because we have other helps to greater brain-power to consider besides Universities, as the Admiralty has other ships to consider besides ironclads.

In the first place, let us inquire if they are equal in number to those of any two nations commercially competing with us.

In the United Kingdom we had until quite recently thirteen.* Of these, one is only three years old as a teaching University, and another is still merely an examining board.

In Germany there are twenty-two Universities; in France, under recent legislation, fifteen; in Italy, twenty-one. It is difficult to give the number in the United States, because it is clear, from the tables given in the Report of the Commissioner of Education, that some colleges are more important than some Universities, and both give the degree of Ph.D. But of Universities in title we have 134. Among these, there are forty-six with more than fifty professors and instructors, and thirteen with more than 150. I will take that figure.

Suppose we consider the United States and Germany our chief commercial competitors, and apply the Admiralty principle. We should require, allowing for population eight additional Universities at the very lowest estimate.

We see, then, that instead of having Universities equalling in number those of two of our chief competitors together, they are by no means equal to those of either of them singly.

After this statement of the facts, anyone who has belief in the importance of higher education will have no difficulty in understanding the origin of the present condition of British industry and its constant decline, first in one direction and then in another, since the tremendous efforts made in the United States and Germany began to take effect.

If, indeed, there be anything wrong about the comparison, the error can only arise from one of two sources—either the Admiralty is thoughtlessly and wastefully spending money, or there is no connection whatever between the higher intelligence and the prosperity of a nation. I have already referred to the views of Mr. Chamberlain and Lord Rosebery on this point; we know what Mr. Chamberlain has done at Birmingham; we know the strenuous efforts made by the commercial leaders of Manchester and Liverpool; we know, also, the opinion of men of science.

If while we spend so freely to maintain our sea-power our export of manufactured articles is relatively reduced because our competitors beat us in the markets of the world what is the end of the vista thus opened up to us? A Navy growing stronger every year and requiring larger votes to guard our commerce and communications, and a vanishing quantity of commerce to guard—a reduced national income to meet an increasing taxation!

The pity is that our Government has considered sea power alone; that while so completely guarding our commerce it has given no thought to one of the main conditions on which its production and increase depend. A glance could have shown that other countries were building Universities even faster than they were building battle ships; were, in fact, considering brain-power first and sea power afterwards.

Surely it is my duty as your President to point out the danger ahead, if such ignoring of the true situation should be allowed to continue. May I express a hope that at

* These are Oxford, Cambridge, Durham, Victoria, Wales, Birmingham, London, St. Andrews, Glasgow, Aberdeen, Edinburgh, Dublin and Royal University.

last, in Mr. Chamberlain's words:—"The time is coming when Governments will give more attention to this matter?"

What will they Cost?

The comparison shows that we want eight new Universities, some of which, of course, will be colleges promoted to University rank, and fitted to carry on University work. Three of them are already named: Manchester, Liverpool, Leeds.

Let us take this number and deal with it on the battleship condition, although a modern University on American or German models will cost more to build than a battleship.

If our present University shortage be dealt with on battleship conditions, to correct it we should expend at least £8,000,000 for new construction, and for the pay-sheet we should have to provide ($8 \times £50,000$) £400,000 yearly for personnel and up-keep; for it is of no use to build either ships or Universities without manning them. Let us say, roughly, capitalising the yearly payment at 2½ per cent, £24,000,000.

At this stage it is important to inquire whether this sum, arrived at by analogy merely, has any relation to our real University needs.

I have spent a year in making inquiries, as full as I could make them, of friends conversant with the real present needs of each of the Universities, old and new. I have obtained statistics which would fill a volume, and personally I believe that this sum at least is required to bring our University system up to anything like the level which is insisted upon both in the United States and in Germany. Even Oxford, our oldest University, will still continue to be a mere bundle of colleges unless three millions are provided to enable the University, properly so called, to take her place among her sisters of the modern world; and Sir Oliver Lodge, the Principal of our very youngest University, Birmingham, has shown in detail how five millions can be usefully and properly applied in that one locality to utilise for the good of the nation the enthusiasm and scientific capacity which are only waiting for adequate opportunity of development.

How is this money to be raised? I reply, without hesitation, *Duplicate the Navy Bill of 1888-9*; do at once for brain-power what we so successfully did then for sea-power.

Let £24,000,000 be set apart from one asset, our national wealth, to increase the other, brain-power. Let it be assigned and borrowed as it is wanted; there will be a capital sum for new buildings to be erected in the next five or ten years, the interest of the remainder to go towards increased annual endowments.

There need be no difficulty about allocating money to the various institutions. Let each University make up its mind as to which rank of the German Universities it wishes to emulate. When this claim has been agreed to, the sums necessary to provide the buildings and teaching staff of that class of University should be granted without demur.

It is the case of battleships over again, and money need not be spent more freely in one case than in the other.

Let me at once say that this sum is not to be regarded as practically gone when spent, as in the case of a short-lived ironclad. *It is a loan* which will bear a high rate of interest. This is not my opinion merely; it is the opinion of those concerned in great industrial enterprises and fully alive to the origin and effects of the present condition of things.

I have been careful to point out that the statement that our industries are suffering from our relative neglect of science does not rest on my authority. But if this be true, then if our annual production is less by only two millions than it might have been, having two millions less to divide would be equivalent to our having forty or fifty millions less capital than we should have had if we had been more scientific.

Sir John Brunner, in a speech connected with the

Liverpool School of Tropical Medicine, stated recently that if we as a nation were now to borrow ten millions of money in order to help science by putting up buildings and endowing professors, we should get the money back in the course of a generation a hundred-fold. He added that there was no better investment for a business man than the encouragement of science, and that every penny he possessed had come from the application of science to commerce.

According to Sir Robert Giffen, the United Kingdom as a going concern was in 1901 worth £16,000,000,000.

Were we to put aside £24,000,000 for gradually organising, building, and endowing new Universities, and making the existing ones more efficient, we should still be worth £15,976,000,000—a property well worth defending by all the means, and chief among these brain-power, we can command.

If it be held that this, or anything like it, is too great a price to pay for correcting past carelessness or stupidity, the reply is that the £120,000,000 recently spent on the Navy, a sum five times greater, has been spent to correct a sleepy blunder, not one whit more inimical to the future welfare of our country than that which has brought about our present educational position. We had not sufficiently recognised what other nations had done in the way of ship-building, just as until now we have not recognised what they have been doing in University building.

Further, I am told that the sum of £24,000,000 is less than half the amount by which Germany is yearly enriched by having improved upon our chemical industries, owing to our lack of scientific training. Many other industries have been attacked in the same way since; but taking this one instance alone, if we had spent this money fifty years ago, when the Prince Consort first called attention to our backwardness, the nation would now be much richer than it is, and would have much less to fear from competition.

Suppose we were to set about putting our educational house in order, so as to secure a higher quality and greater quantity of brain-power, it would not be the first time in history that this has been done. Both Prussia after Jena and France after Sedan acted on the view—

"When land is gone and money spent,
Then learning is most excellent."

After Jena, which left Prussia a "bleeding and lacerated mass," the King and his wise counsellors, among them men who had gained knowledge from Kant, determined, as they put it, "to supply the loss of territory by intellectual effort."

What did they do? In spite of universal poverty, three Universities, to say nothing of observatories and other institutions, were at once founded, secondary education was developed, and in a few years the mental resources were so well looked after that Lord Palmerston defined the kingdom in question as "a country of damned professors."

After Sedan—a battle, as Moltke told us, "won by the schoolmaster"—France made even more strenuous efforts. The old University of France, with its "academies" in various places, was replaced by fifteen independent Universities, in all of which are faculties of letters, sciences, law, and medicine.

The development of the University of Paris has been truly marvellous. In 1897-8 there were 12,000 students, and the cost was £200,000 a year.

But even more wonderful than these examples is the "intellectual effort" made by Japan, not after a war, but to prepare for one.

The question is—Shall we wait for a disaster and then imitate Prussia and France; or shall we follow Japan and thoroughly prepare by "intellectual effort" for the industrial struggle which lies before us?

Such an effort seems to me to be the first thing any national or imperial scientific organisation should endeavour to bring about.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKŁODOWSKA CURIE.

(Continued from p. 99).

CHAPTER II.

METHOD OF RESEARCH.

THE results of the investigation of radio-active minerals, announced in the preceding chapter, led M. Curie and myself to endeavour to extract a new radio-active body from pitchblende. Our method of procedure could only be based on radio-activity, as we know of no other property of the hypothetical substance. The following is the method pursued for a research based on radio-activity:—The radio-activity of a compound is determined, and a chemical decomposition of this compound is effected; the radio-activity of all the products obtained is determined, having regard to the proportion in which the radio-active substance is distributed among them. In this way, an indication is obtained, which may to a certain extent be compared to that which spectrum analysis furnishes. In order to obtain comparable figures, the activity of the substances must be determined in the solid form well dried.

Polonium, Radium, Actinium.

The analysis of pitchblende, with the help of the method just explained, led us to the discovery in this mineral of two strongly radio-active substances, chemically dissimilar:—Polonium, discovered by ourselves, and radium, which we discovered in conjunction with M. Bémont.

Polonium, from the analytical point of view, is analogous to bismuth, and separates out with the latter. By one of the following methods of fractionating, bismuth products are obtained increasingly rich in polonium:—

1. Sublimation of the sulphides *in vacuo*; the active sulphide is much more volatile than bismuth sulphide.
2. Precipitation of solutions of the nitrates by water; the precipitate of the basic nitrate is much more active than the salt which remains in solution.
3. Precipitation by sulphuretted hydrogen of a hydrochloric acid solution, strongly acid; the precipitated sulphides are considerably more active than the salt which remains in solution.

Radium is a substance which accompanies the barium obtained from pitchblende; it resembles barium in its reactions, and is separated from it by difference of solubility of the chlorides in water, in dilute alcohol, or in water acidified with hydrochloric acid. We effect the separation of the chlorides of barium and radium by subjecting the mixture to fractional crystallisation, radium chloride being less soluble than that of barium.

A third strongly radio-active body has been identified in pitchblende by M. Debiere, who gave it the name of *actinium*. Actinium accompanies certain members of the iron group contained in pitchblende; it appears in particular allied to thorium, from which it has not yet been found possible to separate it. The extraction of actinium from pitchblende is a very difficult operation, the separations being as a rule incomplete.

All three of the new radio-active bodies occur in quite infinitesimal amount in pitchblende. In order to obtain them in a more concentrated condition, we were obliged to treat several tons of residue of the ore of uranium. The rough treatment was carried out in the factory; and this was followed by processes of purification and concentration. We thus succeeded in extracting from thousands of kilograms of crude material a few decigrammes of products which were exceedingly active as compared with the ore from which they were obtained. It is obvious that this process is long, arduous, and costly.

Other new radio-active bodies have been notified since the termination of our work. M. Giesel, on the one hand, and MM. Hoffmann and Strauss on the other, have announced the probable existence of a radio-active body

similar to lead in its chemical properties. At present only a few samples of this substance have been obtained.

Radium is, so far, the only member of the new radio-active substances that has been isolated as the pure salt.

Spectrum of Radium.

It was of the first importance to check, by all possible means, the hypothesis, underlying this work, of new radio-active elements. In the case of radium, spectrum analysis was the means of confirming this hypothesis.

M. Demarçay undertook the examination of the new radio-active bodies by the searching methods which he employs in the study of photographic spark spectra.

The assistance of so competent a scientist was of the greatest value to us, and we are deeply grateful to him for having consented to take up this work. The results of the spectrum analysis brought conviction to us when we were still in doubt as to the interpretation of the results of our research.

The first specimens of fairly active barium chloride containing radium, examined by M. Demarçay, exhibited together with the barium lines a new line of considerable intensity and of wave-length $\lambda = 381.47 \mu$ in the ultra-violet. With the more active products prepared subsequently, Demarçay saw the line 381.47μ more distinctly; at the same time other new lines appeared, and the intensity of the new lines was comparable with that of the barium lines. A further concentration furnished a product for which the new spectrum predominated, and the three strongest barium lines, alone visible, merely indicated the presence of this metal as an impurity. This product may be looked upon as nearly pure radium chloride. Finally, by further purification, I obtained an exceedingly pure chloride, in the spectrum of which the two chief barium lines were scarcely visible.

The following is a list, according to Demarçay, of the principal radium lines for the portion of the spectrum included between $\lambda = 500.0$ and $\lambda = 350.0 \mu$. The intensity of each line is represented by a figure, the strongest being marked 16:—

λ .	Intensity.	λ .	Intensity.
482.63	10	460.03	3
472.69	5	453.35	9
469.98	3	443.61	8
469.21	7	434.06	12
468.30	14	381.47	16
464.19	4	364.96	12

All the lines are clear and narrow, the three lines 381.47 , 468.30 , 434.06 are strong, and equal the most intense of those actually known. Two well-marked misty bands are also visible in the spectrum. The first, which is symmetrical, extends from 463.10 to 462.19 , with a maximum at 462.75 . The second, which is stronger, fades towards the ultra-violet; it begins, sharply defined, at 446.37 , and passes through a maximum at 445.52 ; the region of the maximum extends as far as 445.34 , then a nebulous band, gradually fading, extends about as far as 439 .

In the least refrangible part, not photographed in the spark spectrum, the only significant line is 566.5 (approx.), much more feeble, however, than 482.63 .

The general aspect of the spectrum is that of the metals of the alkaline earths; these metals are known to have well-marked line spectra with certain nebulous bands.

According to Demarçay, the position of radium may be among the bodies possessing the most sensitive spectrum reaction. I also have concluded from the work of concentration, that in the first specimen examined, which showed clearly the line 381.47 , the proportion of radium must have been very small (perhaps about 0.02 per cent). Nevertheless, an activity fifty times as great as that of metallic uranium is required in order to distinguish clearly the principal radium line in the spectra photographed. With a sensitive electrometer the radio-activity of a substance only $\frac{1}{10}$ of that of metallic uranium can be detected. It is clear that, in order to detect the presence

* Thesis presented to the Faculté des Sciences de Paris.

of radium, the property of radio-activity is several thousand times more sensitive than the spectrum reaction.

Bismuth containing polonium and thorium containing actinium, both very active, examined by Demarçay, have so far each only yielded bismuth and thorium lines.

In a recent publication, M. Giesel, who is occupied in preparing radium, states that radium bromide gives a carmine flame colouration. The flame spectrum of radium contains two beautiful red bands, one line in the blue-green, and two faint lines in the violet.

Extraction of the New Radio-active Substances.

The first stage of the operation consists in extracting barium with radium from the ores of uranium, also bismuth with polonium and the rare earths containing actinium from the same. These three primary products having been obtained, the next step is in each case to endeavour to isolate the new radio-active body. This second part of the treatment consists of a process of fractionation. The difficulty of finding a very perfect means of separating closely allied elements is well known; methods of fractionation are therefore quite suitable. Besides this, when a mere trace of one element is mixed with another element, no method of complete separation could be applied to the mixture, even allowing that such a method was known; in fact, one would run the risk of losing the trace of the material to be separated.

The particular object of my work has been the isolation of radium and polonium. After working for several years, I have so far only succeeded in obtaining the former.

Pitchblende is an expensive ore, and we have given up the treatment of it in large quantities. In Europe the extraction of this ore is carried out in the mine of Joachimsthal, in Bohemia. The crushed ore is roasted with carbonate of soda, and the resulting material washed, first with warm water and then with dilute sulphuric acid. The solution contains the uranium, which gives pitchblende its value. The insoluble residue is rejected. This residue contains radio-active substances; its activity is four and a-half times that of metallic uranium. The Austrian Government, to whom the mine belongs, presented us with a ton of this residue for our research, and authorised the mine to give us several tons more of the material.

It was not very easy to apply the methods of the laboratory to the preliminary treatment of the residue in the factory. M. Debiere investigated this question, and organised the treatment in the factory. The most important point of his method is the conversion of the sulphates into carbonate by boiling the material with a concentrated solution of sodium carbonate. This method avoids the necessity of fusing with sodium carbonate.

The residue chiefly contains the sulphates of lead and calcium, silica, alumina, and iron oxide. In addition nearly all the metals are found in greater or smaller amount (copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, rare earths, niobium, tantalum, arsenic, barium, &c.). Radium is found in this mixture as sulphate, and is the least soluble sulphate in it. In order to dissolve it, it is necessary to remove the sulphuric acid as far as possible. To do this, the residue is first treated with a boiling concentrated soda solution. The sulphuric acid combined with the lead, aluminium, and calcium passes, for the most part, into solution as sulphate of sodium, which is removed by repeatedly washing with water. The alkaline solution removes at the same time lead, silicon, and aluminium. The insoluble portion is attacked by ordinary hydrochloric acid. This operation completely disintegrates the material, and dissolves most of it. Polonium and actinium may be obtained from this solution; the former is precipitated by sulphuretted hydrogen, the latter is found in the hydrates precipitated by ammonia in the solution separated from the sulphides and oxidised. Radium remains in the insoluble portion. This portion is washed with water, and then treated with a boiling concentrated solution of carbonate of soda. This operation completes the transformation of the sulphates of

barium and radium into carbonates. The material is then thoroughly washed with water, and then treated with dilute hydrochloric acid, quite free from sulphuric acid. The solution contains radium as well as polonium and actinium. It is filtered and precipitated with sulphuric acid. In this way the crude sulphates of barium containing radium and calcium, of lead, and of iron, and of a trace of actinium are obtained. The solution still contains a little actinium and polonium, which may be separated out as in the case of the first hydrochloric acid solution.

From one ton of residue 10 to 20 kilograms of crude sulphates are obtained, the activity of which is from thirty to sixty times as great as that of metallic uranium. They must now be purified. For this purpose they are boiled with sodium carbonate and transformed into the chlorides. The solution is treated with sulphuretted hydrogen, which gives a small quantity of active sulphides containing polonium. The solution is filtered, oxidised by means of chlorine, and precipitated with pure ammonia. The precipitated hydrates and oxides are very active, and the activity is due to actinium. The filtered solution is precipitated with sodium carbonate. The precipitated carbonates of the alkaline earths are washed and converted into chlorides. These chlorides are evaporated to dryness, and washed with pure concentrated hydrochloric acid. Calcium chloride dissolves almost entirely, whilst the chloride of barium and radium remains insoluble. Thus, from one ton of the original material about 8 kilograms of barium and radium chloride are obtained, of which the activity is about sixty times that of metallic uranium. The chloride is now ready for fractionation.

(To be continued).

ALUMINIUM THE CHIEF INORGANIC ELEMENT IN A PROTEACEOUS TREE, AND THE OCCURRENCE OF ALUMINIUM SUCCINATE IN TREES OF THIS SPECIES.*

By HENRY G. SMITH, F.C.S.,
Assistant Curator, Technological Museum, Sydney.

In this paper the author announces the discovery of a flowering plant which uses the element aluminium in large quantities in its construction, and thus differs in this respect from all other Phanerogams. This plant, *Orites excelsa*, R. Br., (N.O. Proteaceae) is one of the "Silky Oaks" of Australia, and occurs plentifully in northern New South Wales and Queensland. It is a tall tree, and reaches a diameter of three feet. A section of a tree from Queensland was exhibited which was three feet in diameter. In the centre of this tree was a large deposit of a basic aluminium succinate of the formula $Al_2(C_4H_4O_4)_3Al_2O_3$. The ash of the wood furthest from the deposit contained 79.61 per cent of alumina, a considerably larger amount than had previously been found in any of the Cryptogams, in which alone aluminium was supposed to occur. This specimen was evidently an abnormal one in regard to the large amount of alumina, and the deposit of aluminium succinate is evidently nature's method of getting rid of an excess of aluminium. Three other samples of the trees of this species from northern New South Wales were investigated, and in the ash of all these large quantities of alumina was found, ranging in amount from 36 to 43 per cent. A large amount of the alumina in the ash was present as an aluminate of potash soluble in water, and as no carbonate of potash was detected it is supposed that the potassium aluminate was originally present in the tree as such. In the ash of the sample from Mullimbimby, cobalt was found, together with 3 per cent of manganese, so that probably cobaltiferous manganese occurs in that locality. Free normal butyric acid was found in the succinate

* A Paper read before the Royal Society of New South Wales, July 1, 1903.

deposit; this was separated and determined by its barium salt; no other volatile acid could be detected. It is evident that the succinic acid is derived from the butyric acid by natural oxidation, and it then probably forms the basic salt with the aluminium in solution. Investigation was made of the ash of *Grevillea robusta*, of *G. Hilliana*, and of *G. striata*, but no alumina could be detected in either, so that the statement previously made (*Proc. Roy. Soc. N.S.W.*, 1895) that aluminium succinate occurred in the timber of *Grevillea robusta* was evidently made in error, and it is probable that the tree from which that deposit was obtained was *Orites excelsa*. When portions of the wood of the Queensland sample were ignited, it was possible to obtain the characteristic cobalt-blue colour for alumina when the ash was moistened with cobalt nitrate and ignited, the other salts being too small in amount to interfere with the reaction.

NOTE ON THE ESTIMATION OF SILICON IN FORGE-IRON.

By GEORGE FREDERICK HORSLEY.

THE great disadvantage of the ordinary nitro-sulphuric acid process for the estimation of silicon in forge-iron lies in the liability towards explosive spurring—at least, this is my experience—towards the end of the preliminary evaporation to dryness. There is also an occasional tendency towards the formation of gelatinous silica. Experiments were therefore made, using various proportions of the three common acids, until a process was devised which is free from both these objections, and which I trust is not well-known already to all my readers.

To 1 grm. of forge-iron add 10 c.c. of dilute H_2SO_4 (1 part acid to 4 parts water) and 15 c.c. of HCl. Boil down till fumes of SO_3 are evolved. Cool, add 100 c.c. water and 10 c.c. HCl, and boil. Filter, and wash once with 5 c.c. HCl and four times with hot water. Dry and ignite.

NOTICES OF BOOKS.

The Alchemist. By BEN JONSON. Edited, with Introduction, Notes, and Glossary, by CHARLES MONTGOMERY HATHAWAY, jun., Ph.D. New York: Henry Holt and Co. 1903.

THIS reprint of Ben Jonson's famous play will owe its interest in the eyes of chemists chiefly to the interesting exposition of the theory and practice of alchemy, which precedes the text; in this description of the predecessor of modern scientific chemistry, its origin, sources, and abuses are fully detailed, with much that is both amusing and instructive with regard to its relations to medicine, astrology, palmistry, and to "all sorts of swindling operations"; in this connection are to be found some astonishing facts relating to modern attempts at deluding the ignorant public into belief in gold-making swindles. The text of the *Alchemist*, which is that of the folio of 1616, is fully annotated with explanatory notes, and well repays critical analysis by the lights it throws on the practices of those who may be regarded as the first chemical investigators.

Grundriss der Reinen und Angewandten Elektrochemie. ("Outlines of Pure and Applied Electrochemistry"). By P. FERCHLAND, Dr. Phil. Halle-a-S.: Wilhelm Knapp. 1903.

THE author of this book states in the preface that in writing it he had in view chiefly the needs of advanced students who already possess a fairly considerable knowledge of physics and chemistry. Such being the case, some parts of the description of simple apparatus and elementary methods, which are always to be found in first text-books of electricity, might well have been omitted as likely to be

perfectly well known by the reader; it appears probable also that it would have been better to introduce the chapters on the theory of solutions and osmotic pressure rather earlier in the volume; but apart from these two points, there is very little to be criticised unfavourably, and on the whole the work may be thoroughly recommended. Though covering much the same ground as many similar works, it has the advantage of being written in a more than usually interesting style, and the striking language of some of the explanations will tend to assist greatly the memory of the student. The illustrations are exceedingly diagrammatic, but both clear and accurate. It is to be regretted that the section on applied electrochemistry is not fuller, some thirty pages only dealing with this branch of the subject.

Selbststrahlende Materie, Atome, und Elektronen. ("Radiant Matter, Atoms, and Electrons"). By Privatdocent Dr. PAUL KÖRNER. Berlin: Julius Springer.

THIS paper, which is a reprint from the *Zeitschrift für Angewandte Chemie*, describes somewhat briefly and in an elementary manner the phenomena of radio-activity, and the recent work of Becquerel, Rutherford, the Curies, and others, with copious references to original publications. Those who have not followed the astonishingly rapid developments of our knowledge of radio-activity will find this summary convenient for use as a basis for further study; at the same time, a greater insistence on the quantitative results which have been obtained would greatly add to its value for all purposes. Though containing nothing absolutely new, the critical examinations of the various theories put forward are unbiased and thoughtful, especially as regards Rutherford's views, with which the author does not always find himself in agreement. Such a paper as this must necessarily have only a more than usually transitory value, but at the same time an occasional review of the present standpoint will certainly be helpful to those who are following with interest the investigations of others, and possibly may suggest new lines of thought or experiment to these latter.

Die Herstellung der Akkumulatoren. ("The Production of Accumulators"). By F. GRÜNWALD. Halle-a-S.: Wilhelm Knapp. 1903.

THE third edition of this handy little book has been brought up to date and made more complete, some parts having been entirely re-written for this purpose. The great advances recently made in the manufacture of accumulators are fully described, with a considerable amount of information relating to the raw materials used for making lead accumulators, their management and applications. There is in places rather a suggestion of the adoption of rule-of-thumb precepts and methods, and the lack of a good index seriously impairs the usefulness of the book, but it appears to give a very full account of the subject, and is well illustrated. A few tables of specific resistance, and the specific gravity and percentage composition of sulphuric acid, &c., are to be found in the appendix.

Elementare Vorlesungen über Telegraphie und Telephonie. 4. Lieferung. ("Elementary Lectures on Telegraphy and Telephony." Part IV.). By Dr. RICHARD HEILBRUN. Berlin: Georg Siemens. 1902.

THIS number of Dr. Heilbrun's Elementary Lectures brings to a conclusion the general part, which is supposed to give students sufficient insight into the more purely scientific sides of physics and chemistry to enable them to understand the theory of telegraphy. In the eleventh lecture rather a sketchy account is given of some of the most important facts of the science of Sound, and the twelfth lecture proceeds to the description of the Morse alphabet and the various modifications of telegraphic apparatus. The previous lectures have already been reviewed in these columns, and there appears nothing to add to, or alter in, the views already expressed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 5, August 3, 1903.

Double Carbide of Chromium and Tungsten.—Henri Moissan and A. Kouznetzow.—The authors prepare by different processes a double carbide of chromium and tungsten of formula $W_2C_3Cr_3C_2$. This double carbide is comparable with the analogous compounds found by MM. Carnot and Goutal in siderurgical products. Its density is 8.41. It is a very stable carbide, and is not attacked by acids and the principal reagents, and is remarkable for its extreme hardness. This latter fact leads the authors to the conclusion that the addition of tungsten to chromated steels may possibly cause the formation of this product, and at the same time produce new and special properties in the steels.

Transformations of Aldehydes and Ketones into Alcohols by Catalytic Hydrogenation.—Paul Sabatier and J. B. Senderens.—The direct action of hydrogen in presence of nickel allows of the easy transformation of formic aldehydes and ketones into the corresponding alcohols. This method has the great advantages over the usual process (action of sodium or sodium amalgam in presence of water)—(1) that there is no accessory product such as pinacone, and (2) during the first process a very good yield of the alcohol is given. The catalytic properties of metals can be employed for the two inverse reactions. On the one hand, reduced copper causes the cleavage of alcohols into hydrogen and aldehydes or ketones, and on the other hand, nickel, in presence of hydrogen at a lower temperature, transforms these latter substances into alcohol.

Estimation of Pyridine in Aqueous Solution.—Maurice François.—The author estimates pyridine in aqueous solution by adding to the solution ready for titration an excess of solution of iodine in potassium iodide, and titrating the iodine left in solution after the deposition of the pyridine periodide. He finds, however, that this method is not very accurate, the pyridine not being entirely precipitated. If, however, he estimates pyridine in the state of the chloraurate very good results are obtained. The details of this estimation are given.

Secondary Amides.—M. Tarbouriech.—The introduction into the molecule of a second radicle causes propionamide to lose the basic character which enables all the primary amides to combine with certain metallic chlorides and picric acid. In the presence of mineral acids the dipropionamide is rapidly hydrolysed with transformation into an ammonia salt.

Reduction of the Ether Salts of Acids of Complex Function.—L. Bouveault and G. Blanc.—The authors reduce the ether salts of non-saturated acids, acid-alcohols, β -ketonic acids, and bibasic acids by means of sodium and absolute alcohol.

Action of Phenylhydrazine on Alcoholic Bromides and Iodides.—J. Allain Le Canu.—Even in alcoholic solution, ethyl bromide can form the bibasic bromhydrate of phenylhydrazine. At the same time, the monobasic bromhydrate and a neutral salt, diethyl bromide of phenylhydrazine, is formed. The same reaction occurs with the iodides of methyl and ethyl, which, with iodides of a higher order, give, in the first place, tribasic iodohydrate of phenylhydrazine. The author also gives the preparation and describes the properties of dipropyl- and diamyl-phenylhydrazine.

Thermochemical Researches on Colouring Matters; Rosaniline and Pararosaniline.—Jules Schmidlin.—The author makes a series of thermochemical researches on the phenomena of neutralisation of colouring matters, and so contributes to the properties of colouring matters in general and of rosaniline and pararosaniline in particular. The slight solubility of rosaniline and its salts necessitates the researches being made with very dilute solutions.

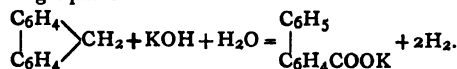
MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information of interest to Students has been received:—

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Head of Chemical Department, Dr. W. H. Mills. Assistants, Mr. W. H. Watson, B.Sc., A.R.C.S., Miss M. A. Bain, M.A., B.Sc., Mr. F. E. Grant, B.Sc. Lectures and Practical Classes in Elementary, Advanced, and Honours Inorganic and Organic Chemistry are held in the evenings from 7 p.m. to 10 p.m., affording instruction in the Courses for the Examinations of the University of London and the Board of Education. The Classes form a Course of Study extending over five Sessions, and are open to both sexes. Large new laboratories and lecture rooms have this Session been added to the Chemical Department, and every facility is afforded for advanced study and research. A reference library is attached to the Chemical Department. Session begins September 22.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Mr. Howard C. Ridding, A.R.S.M., F.I.C.; Vice-Principal, Mr. T. Collins. Chemistry, Assaying, Mineralogy, Magnetism, and Electricity: The Principal. Practical Mining: Capt. W. Hambly, M.E. Mine and Land Surveying, Mechanics, and Geology: Mr. R. H. Watson, B.A., and Mr. R. A. H. Urquhart. Mathematics: Mr. T. Shopland, B.A. Principles of Mining, Ore Dressing, and Technical Drawing: Mr. F. H. Michell, C.E. Steam and Machine Construction and Drawing: Mr. Joseph Blight. Secretary and Registrar: Mr. James A. Winn.

Action of Fused Potash on Fluorene. Synthesis of o-Phenylbenzoic Acid.—M. Weger and K. Döring.—The authors have observed that when fluorene is treated with potash infusion for several hours, a small quantity of acid is formed, which they recognise as o-phenylbenzoic acid; the amount increases as the duration of the time of fusion is longer. This acid, which is obtained from the alkaline filtrate by the addition of sulphuric acid, should be boiled several times with water, to free it from a brown resin present in small quantity. It then separates out in the form of microscopic crystals, fusible at $113.5-114.5^\circ$; this acid is very difficultly soluble in water, but is easily soluble in alcohol, benzene, xylene, and glacial acetic acid. Its copper salt is anhydrous, and corresponds to the formula $(C_{13}H_9O_2)_2Cu$. The acid dissolves easily in the cold, in concentrated sulphuric acid, giving a red colour water precipitates the yellow biphenylene-ketone (fluorenone) directly from this solution; it is fusible at $83-84^\circ$. The secondary reaction which takes place when we melt fluorene with potash, can be expressed by the following equation—



The elimination of hydrogen has been proved. This observation explains why in fusing fluorene with caustic potash, we are able to obtain chemically-pure fluorene, but not fluorene-potassium in the same state; it is for the purpose of confirming the phenomenon that the authors undertook the closer examination of the action of melted potash on fluorene. They found also in the fluorene prepared by the method of fusion with potash, a small quantity of phenanthrene.—*Berichte*, vol. xxxvi., p. 878.

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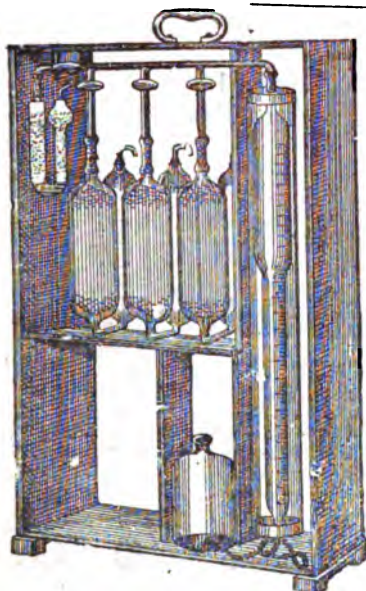
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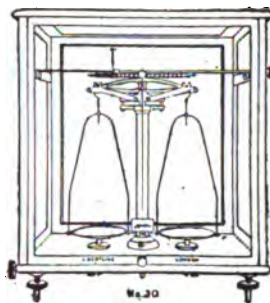
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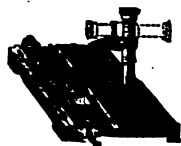
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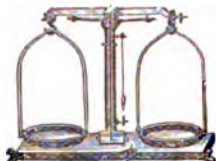
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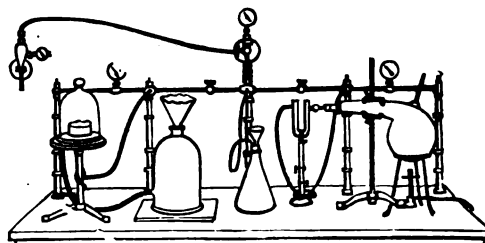
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VOL. LXXXVIII., No. 2286.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTHPORT, 1903.

INAUGURAL ADDRESS OF THE PRESIDENT,

SIR NORMAN LOCKYER, K.C.B., LL.D., F.R.S.,
Correspondant de l'Institut de France.

(Concluded from p. 133).

Research.

WHEN dealing with our Universities I referred to the importance of research, as it is now generally acknowledged to be the most powerful engine of education that we possess. But education, after all, is but a means to the end, which, from the national point of view, is the application of old and the production of new knowledge.

Its national importance apart from education is now so generally recognised that in all civilised nations except our own means of research are being daily more amply provided for all students after they have passed through their University career; and, more than this, for all who can increase the country's renown or prosperity by the making of new knowledge, upon which not only commercial progress, but all intellectual advance must depend.

I am so anxious that my statement of our pressing, and indeed imperative, needs in this direction should not be considered as resting upon the possibly interested opinion of a student of science merely that I must trouble you with still more quotations.

Listen to Mr. Balfour:—

"I do not believe that any man who looks round the equipment of our Universities or medical schools or other places of education can honestly say in his heart that we have done enough to equip research with all the costly armoury which research must have in these modern days. We, the richest country in the world, lag behind Germany, France, Switzerland, and Italy. Is it not disgraceful? Are we too poor or are we too stupid? (*Nature*, May 30, 1901).

It is imagined by many who have given no thought to the matter that this research should be closely allied with some application of science being utilised at the time. Nothing could be further from the truth; nothing could be more unwise than such a limitation.

Surely all the laws of Nature will be ultimately of service, and therefore there is much more future help to be got from a study of the unknown and the unused than we can hope to obtain by continuing the study of that which is pretty well known and utilised already. It was a King of France, Louis XIV., who first commended the study of the *même inutile*. The history of modern science shows us more and more as the years roll on the necessity and advantage of such studies, and therefore the importance of properly endowing them; for the production of new knowledge is a costly and unremunerative pursuit.

Years ago we had Faraday apparently wasting his energies and time in playing with needles; electricity now fills the world. To-day men of science in all lands are studying the emanations of radium; no research could be more abstract; but who knows what advance in human thought may follow or what gigantic world-transforming superstructure may eventually be raised on the minute foundation they are laying?

If we so organise our teaching forces that we can use

them at all stages, from the gutter to the University, to sift out for us potential Faradays—to utilise the mental products which otherwise would be wasted—it is only by enabling such men to continue their learning after their teaching is over that we shall be able to secure the greatest advantage which any educational system can afford.

It is now more than thirty years ago that my attention was specially drawn to this question of the endowment of research—first, by conversations with M. Dumas, the permanent secretary of the Academy of Sciences, who honoured me by his friendship; and, secondly, by my association with Sir Benjamin Brodie and Dr. Appleton in their endeavours to call attention to the matter in this country. At that time a general scheme of endowment suggested by Dumas was being carried out by Duruy. This took the form of the "École spéciale des Hautes Etudes"; it was what our fellowship system was meant to be—an endowment of the research of post-graduate students in each seat of learning. The French effort did not begin then.

I may here tell, as it was told me by Dumas, the story of Léon Foucault, whose many discoveries shed a glory on France and revived French industry in many directions (see *Proc. Roy. Soc.*, vol. xvii., p. lxxxiii.). In 1851, when Prince Napoleon was President of the Republic, he sent for Dumas and some of his colleagues, and told them that during his stay in England, and afterwards in his study of the Great Exhibition of that year, he had found there a greater industrial development than in France, and more applications of science, adding that he wished to know how such a state of things could be at once remedied. The answer was that new applications depended upon new knowledge, and that therefore the most direct and immediate way was to find and encourage men who were likely by research in pure science to produce this new knowledge. The Prince-President at once asked for names; that of Léon Foucault was the only one mentioned during the first interview.

Some time afterwards—to be exact, at about eleven in the morning of December 2—Dumas's servant informed him that there was a gentleman in the hall named Foucault, who wished to see him, and he added that he appeared to be very ill. When shown into the study, Foucault was too agitated to speak, and was blind with tears. His reply to Dumas's soothing questions was to take from his pockets two rolls of banknotes, amounting to 200,000 francs, and place them on the table. Finally, he was able to say that he had been with the Prince-President since eight o'clock that morning, discussing the possible improvement of French science and industry; and that Napoleon had finally given him the money, requesting him to do all in his power to aid the State. Foucault ended by saying that, on realising the greatness of the task thus imposed upon him, his fears and feelings had got the better of him, for the responsibility seemed more than he could bear.*

The movement in England to which I have referred began in 1872, when a society for the organisation of academical study was formed in connection with the inquiry into the revenues of Oxford and Cambridge, and there was a famous meeting at the Freemasons' Tavern, Mark Pattison being in the chair. Brodie, Rolleston, Carpenter, Burdon-Sanderson, were among the speakers, and the first resolution carried was, "That to have a class of men whose lives are devoted to research is a national object." The movement died in consequence of the want of sympathy of the University authorities (see *Nature*, November and December, 1872).

In the year 1874, the subject was inquired into by the

* In order to show how history is written, what actually happened on a fateful morning may be compared with the account given by Kinglake:—"Prince Louis rode home and went in out of sight. Then for the most part he remained close shut up in the Elysée. There, in an inner room, still decked in red trousers, but with his back to the daylight, they say he sat bent over a fireplace for hours and hours together, resting his elbows on his knees, and burying his face in his hands."—"Crimean War," vol. i., p. 245.

late Duke of Devonshire's Commission; and after taking much remarkable evidence, including that of Lord Salisbury, the Commission recommended to the Government that the then grant of £1000, which was expended, by a committee appointed by the Royal Society, on instruments needed in researches carried on by private individuals, should be increased, so that personal grants should be made. This recommendation was accepted and acted on; the grant was increased to £4000, and, finally, other societies were associated with the Royal Society in its administration. The committee, however, was timorous, possibly owing to the apathy of the Universities, and the general carelessness on such matters, and only one personal grant was made; the whole conception fell through.

Meantime, however, opinion has become more educated and alive to the extreme importance of research to the nation, and in 1891, a suggestion was made to the Royal Commission which administers the proceeds of the 1851 Exhibition that a sum of about £6000 a year available for scholarships should be employed in encouraging post-graduate research throughout the whole Empire. As what happened is told in the Memoirs of Lord Playfair, it is not indiscreet in me to state that when I proposed this new form of the endowment of research it would not have surprised me if the suggestion had been declined. It was carried through by Lord Playfair's enthusiastic support. This system has been at work ever since, and the good that has been done by it is now generally conceded.

It is a supreme satisfaction to me to know that in this present year of grace the national importance of the study of the *même inutile* is more generally recognised than it was during the times to which I have referred in my brief survey; and, indeed, we students are fortunate in having on our side in this matter two members of His Majesty's Government, who two years ago spoke with no uncertain sound upon this matter:—

"Do we lack the imagination required to show what these apparently remote and abstract studies do for the happiness of mankind? We can appreciate that which obviously and directly ministers to human advancement and felicity, but seem, somehow or another, to be deficient in that higher form of imagination, in that longer sight, which sees in studies which have no obvious, necessary, or immediate result the foundation of the knowledge which shall give far greater happiness to mankind than any immediate, material, industrial advancement can possibly do; and I fear, and greatly fear, that, lacking that imagination, we have allowed ourselves to lag in the glorious race run now by civilised countries in pursuit of knowledge, and we have permitted ourselves so far to too large an extent to depend upon others for those additions to our knowledge which surely we might have made for ourselves" (Mr. Balfour, *Nature*, May 30, 1901).

"I would remind you that all history shows that progress—national progress of every kind—depends upon certain individuals rather than upon the mass. Whether you take religion, or literature, or political government, or art, or commerce, the new ideas, the great steps, have been made by individuals of superior quality and genius, who have, as it were, dragged the mass of the nation up one step to a higher level. So it must be in regard to material progress. The position of the nation to-day is due to the efforts of men like Watt and Arkwright, or, in our own time, to the Armstrongs, the Whitworths, the Kelvins, and the Siemenses. These are the men who, by their discoveries, by their remarkable genius, have produced the ideas upon which others have acted, and which have permeated the whole mass of the nation and affected the whole of its proceedings. Therefore what we have to do, and this is our special task and object, is to produce more of these great men" (Mr. Chamberlain, *Times*, January 18, 1901).

I finally come to the political importance of research. A country's research is as important in the long run as its battleships. The most eloquent teaching as to its national value we owe to Mr. Carnegie, for he has given the sum of £2,000,000 to found a system of endowments, his chief

purpose being, in his own words, "to secure if possible for the United States of America leadership in the domain of discovery, and the utilisation of new forces for the benefit of man."

Here is a distinct challenge to Britain. Judging by experience in this country, in spite of the magnificent endowment of research by Mond and Lord Iveagh, the only source of possible competition in the British interest is the State, which certainly could not put the 1/8000th part of the accumulated wealth of the country to better use; for without such help both our Universities and our battleships will become of rapidly dwindling importance.

It is on this ground that I have included the importance of endowing research among the chief points to which I have been anxious to draw your attention.

The Need of a Scientific National Council.

In referring to the new struggle for existence among civilised communities I pointed out that the solution of a large number of scientific problems is now daily required for the State service, and that in this and other ways the source and standard of national efficiency have been greatly changed.

Much evidence bearing upon the amount of scientific knowledge required for the proper administration of the public departments, and the amount of scientific work done by and for the nation, was brought before the Royal Commission on Science presided over by the late Duke of Devonshire now more than a quarter of a century ago.

The Commission unanimously recommended that the State should be aided by a scientific council in facing the new problems constantly arising.

But while the home Government has apparently made up its mind to neglect the advice so seriously given, it should be a source of gratification to us all to know that the application of the resources of modern science to the economic, industrial, and agricultural development of India has for many years engaged the earnest attention of the Government of that country. The Famine Commissioners of 1878 laid much stress on the institution of scientific inquiry and experiment designed to lead to the gradual increase of the food supply, and to the greater stability of agricultural outturn, while the experience of recent years has indicated the increasing importance of the study of the economic products and mineral-bearing tracts.

Lord Curzon has recently ordered the heads of the various scientific departments to form a board, which shall meet twice annually, to begin with, to formulate a programme and to review past work. The board is also to act as an advisory committee to the Government (*Nature*, September 4, 1902), providing among other matters for the proper co-ordination of all matters of scientific inquiry affecting India's welfare.

Lord Curzon is to be warmly congratulated upon the step he has taken, which is certain to bring benefit to our great Dependency.

The importance of such a board is many times greater at home, with so many external as well as internal interests to look after—problems common to peace and war, problems requiring the help of the economic as well as of the physical sciences.

It may be asked, What is done in Germany, where science is fostered and utilised far more than here?

The answer is, There is such a council. I fancy, very much like what our Privy Council once was. It consists of representatives of the Ministry, the Universities, the industries, and agriculture. It is small, consisting of about a dozen members, consultative, and it reports direct to the Emperor. It does for industrial war what military and so-called defence councils do for national armaments; it considers everything relating to the use of brain-power in peace—from alterations in school regulations and the organisation of the Universities, to railway rates and fiscal schemes, including the adjustment of duties. I am informed that what this council advises, generally becomes law.

It should be pretty obvious that a nation so provided must have enormous chances in its favour. It is a question of drilled battalions against an undisciplined army, of the use of the scientific spirit as opposed to the hope of "muddling through."

Mr. Haldane has recently reminded us that "the weapons which science places in the hands of those who engage in great rivalries of commerce leave those who are without them, however brave, as badly off as were the dervishes of Omdurman against the maxims of Lord Kitchener."

Without such a machinery as this, how can our Ministers and our rulers be kept completely informed on a thousand things of vital importance? Why should our position and requirements as an industrial and thinking nation receive less attention from the authorities than the headress of the Guards? How, in the words of Lord Curzon (*Times*, September 30, 1902), can "the life and vigour of a nation be summed up before the world in the person of its sovereign" if the national organisation is so defective that it has no means of keeping the head of the State informed on things touching the most vital and lasting interests of the country? We seem to be still in the Palæolithic Age in such matters, the chief difference being that the sword has replaced the flint implement.

Some may say that it is contrary to our habit to expect the Government to interest itself too much or to spend money on matters relating to peace; that war dangers are the only ones to be met or to be studied.

But this view leaves science and the progress of science out of the question. Every scientific advance is now, and will in the future be more and more, applied to war. It is no longer a question of an armed force with scientific corps; it is a question of an armed force scientific from top to bottom. Thank God the Navy has already found this out. Science will ultimately rule all the operations both of peace and war, and therefore the industrial and the fighting population must both have a large common ground of education. Already it is not looking too far ahead to see that in a perfect State there will be a double use of each citizen—a peace use and a war use; and the more science advances, the more the old difference between the peaceful citizen and the man at arms will disappear. The barrack, if it still exists, and the workshop will be assimilated; the land unit, like the battleship, will become a school of applied science, self-contained, in which the officers will be the efficient teachers.

I do not think it is yet recognised how much the problem of national defence has thus become associated with that with which we are now chiefly concerned.

These, then, are some of the reasons which compel me to point out that a scientific council, which might be a scientific committee of the Privy Council, in dealing primarily with the national needs in times of peace, would be a source of strength to the nation.

To sum up, then. My earnest appeal to you is to gird up your loins and see to it that the science of the British Empire shall no longer remain unorganised. I have endeavoured to point out to you how the nation at present suffers from the absence of a powerful, continuous, reasoned expression of scientific opinion, urging in season and out of season that we shall be armed as other nations are, with efficient Universities and facilities for research to uphold the flag of Britain in the domain of learning and discovery, and what they alone can bring.

I have also endeavoured to show how, when this is done, the nation will still be less strong than it need be if there be not added to our many existing councils another, to secure that even during peace the benefits which a proper co-ordination of scientific effort in the nation's interest can bring shall not be neglected as they are at present.

Let some of you may think that the scientific organisation which I trust you will determine to found would risk success in working on such large lines, let me remind you that in 1859, when the late Prince Consort occupied this

Chair, he referred to "impediments" to scientific progress, and said, "they are often such as can only be successfully dealt with by the powerful arm of the State or the long purse of the nation."

If the Prince Consort had lived to continue his advocacy of science, our position to-day would have been very different. His early death was as bad for Britain as the loss of a great campaign. If we cannot make up what we have lost, matters cannot mend.

I have done what I feel to be my duty in bringing the present condition of things before you. It is now your duty, if you agree with me, to see that it be put right. You can if you will.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

SOUTHPORT, 1903.

By Professor W. N. HARTLEY, D.Sc., F.R.S., F.R.S.E.,
President of the Section.

THE oftentimes laborious method of investigating the relationship of substances by ascertaining how one form of matter can operate upon another—in other words, by chemical reactions—has of late years been supplemented by the examination of their physical properties, and has been extended to compounds, both organic and inorganic. In several directions this has led to results of very uncommon interest. Accordingly I propose to offer a brief account of twenty-five years' experimental work in that branch of chemical physics which deals with the emission and absorption of rays of measurable wave-length, and to review its present position chiefly in relation to the theory of chemistry, indicating where it may be usefully and profitably extended.

According to Davy ("Chemical Philosophy," 1812, vol. i., p. 211), Ritter observed chemical action on moist chloride of silver to be different in different parts of the spectrum, slight in the red, greater towards the violet, and extending into a space beyond the violet where there is no sensible light or heat. Wollaston discovered that chemical action was exerted by refracted rays in a region where they were of a higher refrangibility than any rays that were visible. Young showed that the invisible rays are liable to the same affections as visible rays. Hence we have the beginnings of spectrum analysis in its chemical relations to terrestrial matter, in the infra-red, the visible, and the ultra-violet regions.

Everyone is more or less familiar with the subject of spectrum analysis. This was defined by Tait as an optical method of making a diagnosis of the chemical composition of either (a) a self-luminous body, or (b) an absorbing medium, whether self-luminous or not. It has now become necessary to enlarge this definition, and I would suggest that it is the study of the composition and the constitution of matter by means of radiant energy, and recording in the order of their refrangibilities the rays emitted and absorbed by matter. By this modified statement the infra red or so-called "invisible heat rays," the visible or "colour rays," and the ultra-violet or "chemical rays" are included.

Spectra are of two kinds, emission and absorption spectra. It will be convenient if the latter are considered first.

ABSORPTION SPECTRA.

The Infra-red Region.

Abney (1880) by the preparation of a particularly sensitive form of collodion emulsion containing silver bromide was successful in obtaining very extraordinary results. Such films as he prepared were so sensitive to invisible radiations of long wave-length as to be capable of forming a representation of even a kettle of boiling water standing in an absolutely dark room. This picture could not of course be properly referred to as a photograph,

though the process by which it was obtained was such as we are accustomed to term a photographic process. It may with greater propriety be termed an actinograph, the result not of light, but of dark rays. The least refrangible of the visible rays lies about wave-length 7800 ten-millionths of a millimetre, or Angström units; but these rays extend as far as wave-length 12,000, while Becquerel has measured lines in the spectra of metals of as low a refrangibility as wave-length 18,000.

Abney and Festing (1881) investigated the influence of atomic groupings in the molecules of organic substances by measuring their absorption in the infra-red region of the spectrum.

They studied such simply constituted substances as water, hydrochloric acid, chloroform, carbon tetrachloride, and cyanogen, besides many hydrocarbons with their hydroxyl, haloid, and carboxyl derivatives. Characteristic groups of lines or very narrow bands were observed in carbon compounds, but they are absent from carbon compounds, containing no hydrogen, and do not all appear in some of the hydrogen compounds. The facts observed led to the conclusion that they belonged to hydrogen, but are subject to some occasional modifications. Oxygen in hydroxyl, for instance, modifies two of the lines, since it obliterates by absorption the rays which lie between them. Oxygen in aldehyde, or when it forms part of the carbon nucleus of some such compound, presents bands which are bounded by well-defined lines, or are inclined to be linear. These appear to be characteristic bands indicating the carbon nucleus of a series of substances. Alkyl radicals, such as ethyl, exhibit absorption bands, and so does the benzene nucleus. It is a remarkable fact that bands appear in the solar spectrum which correspond with those of benzene (1881).

Julius (1893) has investigated the absorption in the infra-red caused by many carbon compounds by means of the bolometer, combined with a prism, and also with a diffraction grating. He showed that the molecules of compound substances absorbed the rays which were emitted at the time of their formation. Thus, to take the simplest case, the emission spectrum of hydrogen burning in air corresponds with the absorption bands of water vapour; that is to say, the absorption spectra of the compounds are the counterpart of the emission spectra of the flames which yield these compounds during combustion. The emission spectrum of carbon dioxide is found in the spectrum of burning carbon monoxide, cyanogen, methane, and carbon disulphide; and that of water vapour in various hydrocarbons. As early as 1888 Julius, in an Inaugural Dissertation, quoting Tyndall, recognised that the absorption and emission of rays measured with the thermopile were manifestations of the molecular vibrations.

The various absorption spectra examined included those of the alcohols, such as isopentyl, isobutyl, normal butyl, propyl, ethyl, and methyl, as well as hydrocarbons, chloroform, and benzene. The study of the maxima of radiation and the maxima of absorption offers us a means of arriving at a knowledge of a series of new and valuable physical constants, namely, the vibration periods characteristic of the molecules. (Tyndall discussed this subject in his usually luminous style on pages 391 to 402 of his work "Heat as a Mode of Motion").

Puccianti (1900) has examined the infra-red absorption spectra of liquids, including aromatic compounds and alkyl derivatives, while Donath has examined in the same region various essential oils. Carbon combined with hydrogen shows a maximum of absorption with a wave-length about (1.71μ m.m.) 17,100 Angström units.

Benzene and pyridine have two other maxima of absorption in common. The alcohols have very similar maxima of absorption at wave-length 21,000.

The three isomeric xylenes show absorption spectra which are almost identical. At or about wave-length 23,200 another maximum of absorption is shown.

Julius refers to Langley's observation that at a wave-length of 27,000 there is an abrupt termination to the solar

spectrum, probably caused by the water vapour in the atmosphere; but a band extends to 273,000, and at no very great elevation above the earth's surface there are rays with a wave-length of 45,700 Angström units. All radiations of longer wave-length—and Julius has measured down to 149,000 Angström units—are likely to be absorbed by the carbon dioxide in the atmosphere.

The Visible Rays or Colour Region.

J. L. Schönn (1879) examined the absorption spectra of substances usually considered to be colourless in layers from 1.6 to 3.7 metres in thickness and observed narrow bands in the spectra of methyl, ethyl, and amyl alcohol, lying in the red, orange, and yellow; methyl alcohol showed two bands, ethyl and amyl alcohol each three. Gerard Krüss (1888) calculated the wave-lengths of these bands, and it appears that the higher members of the homologous series have the bands displaced towards the red end of the spectrum. Russell and Lapraik (1879) made similar observations on columns of liquid from two to eight feet in length. All the substances gave well-defined absorption bands lying between wave-lengths 6000 and 7000.

The bands of the different substances differed altogether from the bands of water. Alcohols give a band which is similar in different alcohols, but the higher the alcohol stands in the homologous series—that is to say, the larger the number of carbon atoms it contains—the nearer is the band to the red end of the spectrum (1881).

It was definitely established that for each CH_3 introduced into a molecule of ammonia or benzene there is a shifting of the absorption bands towards the red end of the spectrum.

It will, of course, be understood that the liquids examined were perfectly colourless in the ordinary acceptance of the term; and that they appear so is owing to the bands of absorption being very narrow, so that the percentage of luminous rays withdrawn by absorption is but a very small fraction of the whole spectrum emitted by a source of light when viewed under ordinary conditions.

Numerous observations were made by Melde, Burger, Magnus, H. W. Vogel, and Landauer (1876-78), which showed that changes in the absorption spectra of solutions are partly physical and partly chemical; that is to say, they are caused by changes in the constitution of the solution. Vogel mentions cases where no chemical change was believed to take place, as, for instance, where naphthalene red shows different spectra according to whether it is dissolved in alcohol, water, resin, or is solid or used to colour paper (1878).

This points to some difference in the constitution of the solution. A well-known instance is that of iodine in alcohol, chloroform, or carbon disulphide.

It must be observed that Vogel's work referred merely to phenomena observable in the visible spectrum, to small thicknesses of the absorbing medium, and was not applied quantitatively. Two solutions may give spectra which are apparently identical at one concentration, but spectra quite different when submitted to varying degrees of dilution.

In order to ascertain in what way absorption spectra are related to the chemical constitution of organic substances, it is necessary to examine a wider range of spectrum than that included in the merely visible region, and this may be done by extending the observations into the ultra-violet.

The Ultra-violet Region.

Stokes in preparing his experiments for a Friday evening discourse at the Royal Institution observed that the spectrum of electric light when a prism and lenses of quartz were used extended no less than six or eight times the length of the visible spectrum. In 1862 he studied the ultra-violet spectra of metals and executed drawings of the lines exhibited by aluminium, zinc, and cadmium. He discovered the fact that certain solutions show light and dark bands in the spectrum of rays transmitted by them, the solutions being colourless; the bands are invisible

unless they fall on a fluorescent screen. It was under such conditions that they exhibited light and darkness. The screen used was of plaster-of-Paris saturated with a fluorescent substance, such as uranium phosphate.

William Allen Miller in 1863, simultaneously with Stokes, described his method of examining the photographic transparency of various saline solutions and organic substances and of depicting metallic spectra. A sensitised photographic plate was used for the reception of the rays of the spectrum, so that they were made to register their own position and intensity. L. Soret invented the fluorescent eye-piece for the purpose of investigating the ultra-violet rays, and ascertained the best media for the transmission of rays of high refrangibility. Colourless fluor-spar, a rare mineral, was found to answer best, and quartz lenses were achromatised with this. Iceland spar was found to absorb some of the more refrangible rays, and a pure spectrum was difficult to obtain with quartz prisms owing to double refraction, which caused the lines in metallic spectra to be duplicated. Struck by the fact that Miller had examined many organic substances without obtaining evidence of a connection between their constitution and their absorption spectra—the actual words used by Miller were, "I have not been able to trace any special connection between the chemical complexity of a substance and its diacritic power" (*Journ. Chem. Soc.*, vol. xi., p. 68)—it appeared to me desirable that this point should be systematically re-investigated. L. Soret had already proceeded with work in this direction, by examining and drawing a great variety of organic substances and diagrams of absorption curves. But it was deemed necessary to make a large number of examinations of substances of a comparatively simple constitution, and according to theory closely related, and afterwards gradually to proceed to the study of substances of greater complexity. For such purposes a photographic method alone appeared a practicable one, particularly when comparisons had to be made between substances observed at different times, for the reason that none but photographic records could be absolutely relied upon and stored away for future reference.*

The plan of the proposed investigation was to photograph the rays transmitted by molecular proportions of hydrocarbons, alcohols, acids, and esters, either alone as vapour or liquid, or dissolved in some neutral and, in comparison with the substances to be examined, an optically non-absorbent solvent.

It was considered that the metameric esters would afford much information if a sufficient number of them were examined and their spectra compared, and if the acids themselves were not responsive the sodium and potassium

salts in solution would serve the purpose, since the alkalis did not affect the spectrum. The general deductions (1879) are now well known, but two points not generally taken into account were well established. First, the extraordinary delicacy of the ultra-violet spectrum in detecting traces of impurities. For instance, pyridine, an invariable impurity in commercial ammonia, is present in the proportion of about $\frac{1}{1000}$ th. It was proved that the absorption spectra of the normal paraffins, prepared with the greatest care by Schorlemmer, contained traces of impurities which could not be separated. Secondly, some of the normal alcohols could not be rendered pure by the ordinary methods employed, and great care was necessary in their preparation. It may well be asked that, if such were the case, upon what grounds was it concluded that impurities were present? How was it possible to distinguish between a normal and an abnormal absorption spectrum when no standards of comparison existed? It may be of interest if this question be now answered, as no adequate account of it has been made public. All the substances in any one homologous series were shown to vary in the extent to which the rays at the more refrangible end of the spectrum were absorbed, and the different terms of the series differ solely by the number of CH_2 groups in the molecule; and the greater the number of these the greater the absorption. The extent of the absorption should be proportional to the molecular weight of the substance. Accordingly, if repeatedly purifying and fractionally distilling a considerable quantity of material failed to give spectra which were constant and identical, but gave instead spectra which were variable, even in a slight degree, it was evident that the absorption due to the molecule of the substance was interfered with by some impurity.

When, however, it became evident that successive quantities of methyl alcohol, for example, prepared in a certain manner yielded spectra which were practically identical under different conditions, such as thickness of liquid, and that they differed but slightly from that of pure water after the type of which the alcohol is constituted, the conclusion was inevitable that we were dealing with a pure preparation. In short, the longest spectrum obtained under all circumstances and under every reasonable condition could not possibly be the result of accident, more particularly if it could be repeatedly obtained from different specimens of the same substance. The same reasoning applies to the acids and their salts in the investigation of which similar difficulties arose.

Soret and Rilliet pointed out that in the rectification and prolonged desiccation of the alcohols there is often slight oxidation which leads to the production of impurities which affect the spectra transmitted by them.

They found that ethyl alcohol is not appreciably less diacritic than methyl alcohol, and both transmitted a spectrum nearly as long as that of water. This was shown by Huntington and me when the usual 25 m.m. of thickness of the layer of liquid were tested. By taking columns of liquid 100 m.m. in length the differences are greater, and they increase with columns of increased length.

The influence of each additional CH_2 in the molecule causes a shortening of the spectrum. This was shown to be due to the carbon atoms and not to the hydrogen. The acids, containing the same number of carbon atoms as the alcohols, have a much greater absorptive power, which is due to the carboxyl group ($\text{C}\cdot\text{O}\cdot\text{OH}$). By the examination of a number of various substances, such as polyhydric alcohols, as glycol, glycerol, mannitol, and various sugars, it was found that, no matter what its complexity, no open-chain compound causes selective absorption, i.e., absorption bands.

Shortly it may be stated that in the examination of organic substances we have three variations in absorption spectra:—First, those of substances the rays of which are freely transmitted, the absorption being at the more refrangible end of the spectrum, and the spectrum of which is readily increased in length by dilution; secondly, those

* Clerk Maxwell had calculated for Miller the best focal length of lenses of quartz which would give an approximately flat field. His computation made this something over a length of three feet. All Miller's photographs were taken with the plate placed normal to the axis of the lens, but Stokes had shown that the locus of the foci of the different rays formed an arc of a curve or nearly a straight line, lying very obliquely to the axes of the pencils coming through the lens.

It was obvious from Miller's photographs that only one or two rays on each plate were even approximately in focus. To obtain spectra in focus from end to end it was evidently necessary to incline the plate so that the end upon which the red rays would fall, which are of longest wave-length, should be farther off than that upon which the ultra-violet fall, which are of shortest wave-length. It was also found experimentally that lenses of much shorter focal length (10 or 12 inches) could be used, giving perfect definition, and, what is still more important, it was found a positive advantage not to have them corrected by fluor-spar or calcite. The plate carrier was adjusted at an inclination of approximately 22° to the normal; in such a position the rays from the yellow sodium line to the extreme ultra-violet of the spark spectrum of cadmium were simultaneously in focus on a plane surface.

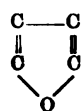
The prism was of quartz cut on Cornu's plan, the method of construction designed to get rid of all double refraction being communicated to me by M. Cornu in a very kindly written letter. The first instrument was constructed in 1878 and the description of it published in 1881. It has been the model for several others. One with two prisms and lenses of 12 inches focus was exhibited by me in the Inventions Exhibition in 1882. At the Jubilee Meeting of the British Association at York the spark spectra of iron, cobalt, and nickel, enlarged to twenty-five diameters and printed by the Autotype Company, were exhibited. They are over 8 feet in length, and have proved very useful for reference. The photographic process is a point of great importance; the then newly invented gelatin bromide films made by Kennet were alone quite suitable.

in which the spectra are of the same kind, but the absorptive power is greater, so that they withstand dilution to a much greater extent; thirdly, those spectra which exhibit selective absorption, and which at the same time exert great absorptive power, or, in other words, can undergo great dilution before the absorption bands are rendered visible, and still further dilution before they are extinguished or obliterated.

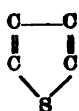
Spectra of the First Variety belong to substances which are constructed on an open chain of carbon atoms, thus:— $C-C-C-C$ or $C=C-C-C$ and $C\equiv C-C-C$.

The introduction in place of one or more atoms of hydrogen—of hydroxyl, OH, carboxyl, COOH, methoxyl, OCH_3 , CO, COH, or NH_2 , or of side chains such as CH_3 , C_2H_5 , &c.—does not affect the character of the spectra, but merely the absorptive power, which is increased when oxygen or an oxygenated radical is introduced.

Spectra of the Second Variety are spectra of substances so constituted that the carbon atoms form a closed chain. It is immaterial whether the closed chains are homocyclic or heterocyclic; thus:—



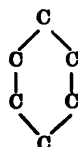
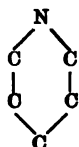
Furfuran.



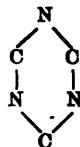
Thiophene.



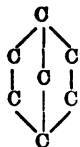
Pyrrol.

Diketohexamethylene
Hydro-aromatic
compounds.

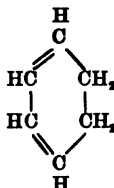
Piperidina.



Cyanuric Acid.



Camphor.



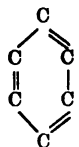
Dihydrobenzene.



Cineol.

They possess greater absorptive power than open-chain compounds, but do not exhibit absorption bands. It is manifestly the chain or ring structure of the compounds that gives them greater absorptive power, and not the number of carbon atoms in the molecules.

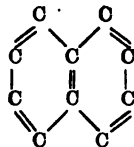
Spectra of the Third Variety.—These show absorption bands, and the substances yielding them are generally constituted on the type of benzene, naphthalene, anthracene, phenanthrene, &c.; but the rings may be either homocyclic or heterocyclic without the character of the spectra being altered; thus:—



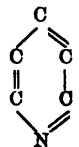
Benzene.



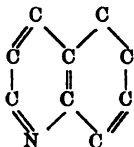
Benzenes.



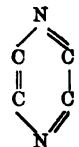
Naphthalene.



Pyridine.



Quinoline.



Pyrazine.

If we say that the compounds which are homocyclic are constituted of at least three pairs of carbon atoms doubly linked, which are themselves singly linked together, we may make use of the formula of Kekulé for benzene as the simplest expression of their constitution; if we assume that each of the six atoms is linked to at least other two atoms we adopt what is practically the prism formula of Ladenburg, or the same idea expressed in space of two dimensions. It is difficult to express the physical condition by the Armstrong-Baeyer formula or centric arrangement because this does not clearly suggest to one's mind what is manifestly the fact, namely, that the carbon atoms in the nucleus of benzene are much more closely condensed or combined to-

gether than those of the hydroaromatic series. This condensed condition of the carbon atoms is evident from the higher molecular refractive energy of aromatic compounds and of the specific refractive energy of the carbon in such combinations.

Side chains such as do not exert selective absorption have no influence on the character of the spectra, but they slightly increase the general absorption.

Heterocyclic compounds possess greater absorptive power, both as regards the general and selective absorption, than those which are homocyclic.

The point which I particularly desire to draw attention to here is, that for the first time Kekulé's remarkable benzene theory was supported by definite physical measurements, and the closed-ring formula represented a veritable actuality.

Of Molecular and Intra-molecular Vibrations.

Johnstone Stoney was the first to show that the cause of the interrupted spectra of gases is to be referred to the motions within the individual molecules and not to the

irregular journeys or encounters of the molecules with each other; and this applies to the absorption as well as to emission spectra. He further advised the use of oscillation frequencies instead of wave-lengths in describing the measurements of spectra. Johnstone Stoney and Emerson Reynolds subsequently examined the extraordinary absorption exhibited by chlorochromic anhydride, the bands in which are evidently harmonically related.

It has already been shown that the hydrocarbons of the aromatic series exert two kinds of absorption, a general and a selective absorption. All the evidence we possess war-

rants the belief that the general absorption is caused by the motion of the molecules, while the selective absorption is due to the motion within the molecules.

When the molecule of a substance is capable of vibrating synchronously with a radiation, the ray received on this substance is absorbed. The absorption is complete if the direction of the vibration of the molecule and of the ray is the same but the phase opposite, and if the number of molecules in the path of the rays is sufficient to damp all the vibrations.

When the quantity of substance in the path of the rays is reduced, the number of molecules present is not sufficient to damp all the vibrations, and some of the rays are trans-

mitted. If, however, certain carbon atoms within the molecule are vibrating synchronously with certain rays, we shall have selective absorption of these rays after the general absorption has been so weakened by dilution or otherwise as to allow them to pass.

It is evident, then, that general selective absorption exerted by carbon compounds is due to the vibration of the molecules because the absorption increases with the number of carbon atoms in the molecule; or, in other words, in any homologous series the greater the molecular mass the lower the rate of vibration of the molecule.

It has not been found possible to associate any of the absorption bands of the substances examined with any particular carbon atoms; but the bands in benzene are six in number, or the same in number as the carbon atoms. It has, however, been shown that the rapidity of the intramolecular vibrations was dependent upon the rate of vibration of the molecules. From numbers representing approximately the mean wave-lengths of the four chief bands of rays absorbed by benzene, naphthalene, and anthracene, and from the velocity of light, the mean rate of the vibrations within the molecules was calculated (1881), the numbers being as follows:—

	Molecular vibrations.
Benzene	1248 ¹⁰
Naphthalene	1177 ¹⁰
Anthracene	910 ¹⁰

The mean rate of vibration of the rays absorbed by naphthalene is less than that absorbed by benzene, and those of anthracene less than those of naphthalene. It follows from this that the vibrations within the molecules are not independent, but are a consequence, of the fundamental molecular vibrations, like the harmonics of a stretched string or of a bell.

The term absorptive power has generally been used with respect to the extent of rays of the spectrum absorbed, but there is intensity of absorption to be considered. In the case of a vibrating string or tuning-fork greater amplitude of vibration means a louder note; in the case of molecules greater intensity of absorption may be caused by a greater amplitude of vibration in the molecules of the absorbing medium, the number of molecules being constant. But by greater amplitude it is not to be understood that the rate of vibration is increased.

If this be so then, as the absorption intensity of anthracene and naphthalene is, molecule for molecule, greater than that of benzene, the amplitude of vibration of the molecules of these substances is greater, but the rate of vibration is slower.

From the foregoing it will be observed that where λ is the wave-length $\frac{1}{\lambda}$ is the inverse wave-length, and, omitting the correction for the refraction of air, which is a very small value, it is the oscillation frequency of the ether in a small unit of time, and the most convenient measurement for use in describing spectra. Seven years after the publication of these views, Gerard Krüss (1888) dealt with the subject of coloured substances in a similar manner. From the undulatory theory of light, deductions may be drawn regarding the inner molecular movements or interatomic movements within the molecules, inasmuch as the vibrations of the ether, which fills the intra-molecular space, are a resultant within that space of the velocity and amplitude of the molecular vibrations.

Thus, if λ be the wave-length of a ray emitted by a substance, and v the velocity of light, the number of vibrations, n , which a molecule sends forth by movements of it as a whole and of its parts can be determined by the equation

$$n = \frac{v}{\lambda}.$$

G. Krüss made a series of calculations for coloured substances similar to those which I had made for colourless substances and for ozone.

Curves of Molecular Vibrations.

Observations on absorption spectra should, whenever it is possible, be made with reference to the quantity of substance which produces a given measurable effect. A molecular weight in milligrams. or a milligram-molecule is a convenient quantity which may be dissolved in 20 c.c., 40 c.c., or 100 c.c. of any non-absorbent liquid, and observed through thicknesses of the solution varying from 25 m.m. to 1 m.m. in thickness. When a series of photographs have been measured a curve is plotted, which shows the general and the selective absorption of the substance. The oscillation frequencies of the absorbed rays are taken as abscissæ, and the proportional thickness in millimetres of the weakest of a series of solutions as ordinates. The curves are as often as possible made continuous, and they are called *curves of molecular vibrations*.

The curves of the molecular vibrations present very striking features: they are valuable physical constants which enable one to classify and identify substances.

Position Isomerism.

Isomerides of the *ortho*-, *meta*-, and *para*-positions in aromatic substances yield spectra with the absorption bands, differing in position, in width, and in intensity. There is no distinguishing character to be observed in the different isomerides. Isomerism in the pyridine, quinoline, and naphthalene derivative has not yet been completely studied. In such cases as have already passed under review there is nothing that indicates the positions of the substituted hydrogens.

Stereo-isomerism.

Where isomerism is not due to differences in structure, but simply to the distribution of the atoms in space, we have no means of distinguishing isomeric substances from an examination of their spectra; for instance, *benz-syn-aldoxime* and *benz-anti-aldoxime* yield curves of molecular vibrations which are identical.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKŁODOWSKA CURIE.

(Continued from p. 135).

CHAPTER II. (continued).

Polonium.

As I said above, by passing sulphuretted hydrogen through the various hydrochloric acid solutions obtained during the course of the process, active sulphides are precipitated, of which the activity is due to polonium. These sulphides chiefly contain bismuth, a little copper and lead; the latter metal occurs in relatively small amount, because it has been to a great extent removed by the soda solution, and because its chloride is only slightly soluble. Antimony and arsenic are found among the oxides only in the minutest quantity, their oxides having been dissolved by the soda. In order to obtain the very active sulphides, the following process was employed:—The solutions made strongly acid with hydrochloric acid were precipitated with sulphuretted hydrogen; the sulphides thus precipitated are very active, and are employed for the preparation of polonium; there remain in the solution substances not completely precipitated in presence of excess of hydrochloric acid (bismuth, lead, antimony). To complete the precipitation, the solution is diluted with water, and treated again with sulphuretted hydrogen, which gives a second precipitate of sulphides, much less active than the first, and which have generally been rejected. For the further purification of the sulphides, they are washed with ammonium sulphide, which removes the last remaining

* Thesis presented to the Faculté des Sciences de Paris.

traces of antimony and arsenic. They are then washed with water and ammonium nitrate, and treated with dilute nitric acid. Complete solution never occurs; there is always an insoluble residue, more or less considerable, which can be treated afresh if it is judged expedient. The solution is reduced to a small volume and precipitated either by ammonia or by excess of water. In both cases the lead and the copper remain in solution; in the second case, a little bismuth, scarcely active at all, remains also in solution.

The precipitate of oxides or basic nitrates is subjected to fractionation in the following manner:—The precipitate is dissolved in nitric acid, and water is added to the solution until a sufficient quantity of precipitate is formed; it must be borne in mind that sometimes the precipitate does not at once appear. The precipitate is separated from the supernatant liquid, and re-dissolved in nitric acid, after which both the liquids thus obtained are re-precipitated with water, and treated as before. The different fractions are combined according to their activity, and concentration is carried out as far as possible. In this way is obtained a very small quantity of a substance of which the activity is very high, but which, nevertheless, has so far only shown bismuth lines in the spectroscopic.

There is, unfortunately, little chance of obtaining the isolation of polonium by this means. The method of fractionation just described presents many difficulties, and the case is similar with other wet processes of fractionation. Whatever be the method employed, compounds are readily formed which are absolutely insoluble in dilute or concentrated acids. These compounds can only be re-dissolved by reducing them to the metallic state, *e.g.*, by fusion with potassium cyanide. Considering the number of operations necessary, this circumstance, constitutes an enormous difficulty in the progress of the fractionation. This obstacle is the greater because polonium, once extracted from the pitchblende, diminishes in activity. This diminution of activity is slow, for a specimen of bismuth nitrate containing polonium only lost half its activity in eleven months.

No such difficulty occurs with radium. The radio-activity remains throughout an accurate gauge of the concentration; the concentration itself presents no difficulty, and the progress of the work from the start can be constantly checked by spectral analysis.

When the phenomena of induced radio-activity, which will be discussed later on, were made known, it seemed obvious that polonium, which only shows the bismuth lines and whose activity diminishes with time, was not a new element, but bismuth made active by the vicinity of radium in the pitchblende. I am not sure that this opinion is correct. In the course of my prolonged work on polonium, I have noted chemical effects, which I have never observed either with ordinary bismuth or with bismuth made active by radium. These chemical effects are, in the first place, the extremely ready formation of insoluble compounds of which I have spoken above (especially basic nitrates), and, in the second place, the colour and appearance of the precipitates obtained by adding water to the nitric acid solution of bismuth containing polonium. These precipitates are sometimes white, but more generally of a more or less vivid yellow, verging on red.

The absence of lines other than those of bismuth does not necessarily prove that the substance only contains bismuth, because bodies exist whose spectrum reaction is scarcely visible.

It would be necessary to prepare a small quantity of bismuth containing polonium in as concentrated a condition as possible, and to examine it chemically, in the first place determining the atomic weight of the metal. It has not yet been possible to carry out this research on account of the difficulties of a chemical nature already mentioned.

If polonium were proved to be a new element, it would be no less true that it cannot exist indefinitely in a strongly

radio-active condition, at least when extracted from the ore. There are therefore two aspects of the question:—First, whether the activity of polonium is entirely induced by the proximity of substances themselves radio-active, in which case polonium would possess the faculty of acquiring atomic activity permanently, a faculty which does not appear to belong to any substance whatever; second, whether the activity of polonium is an inherent property, which is spontaneously destroyed under certain conditions, and persists under certain other conditions, such as those which exist in the ore. The phenomenon of atomic activity induced by contact is still so little understood, that we lack the ground on which to formulate any opinion on the matter.

(NOTE.—A work has recently appeared on polonium by M. Marckwald. He plunges a small rod of pure bismuth into a hydrochloric acid solution of the bismuth extracted from the pitchblende residue. After some time the rod becomes coated with a very active deposit, and the solution now contains only inactive bismuth. M. Marckwald also obtains a very active deposit by adding tin chloride to a hydrochloric acid solution of radio-active bismuth. From this he concludes that the active element is allied to tellurium, and gives it the name of *radiotellurium*. This active substance of M. Marckwald seems identical with polonium, from its behaviour, and from the easily absorbed rays it emits. The choice of a new name for this substance is futile in the present state of the question).

Preparation of the Pure Chloride of Radium.

The method by which I extracted pure radium chloride from barium chloride containing radium consists in first subjecting the mixture of the chlorides to fractional crystallisation in pure water, then in water to which hydrochloric acid has been added. The difference in solubility of the two chlorides is thus made use of, that of radium being less soluble than that of barium.

At the beginning of the fractionation, pure distilled water is used. The chloride is dissolved, and the solution raised to boiling-point, and allowed to crystallise by cooling in a covered capsule. Beautiful crystals form at the bottom, and the supernatant, saturated solution is easily decanted. If part of this solution be evaporated to dryness, the chloride obtained is found to be about five times less active than that which has crystallised out. The chloride is thus divided into two portions, A and B—portion A being more active than portion B. The operation is now repeated with each of the chlorides A and B, and in each case two new portions are obtained. When the crystallisation is finished, the less active fraction of chloride A is added to the more active fraction of chloride B, these two having approximately the same activity. Thus there are now three portions to undergo afresh the same treatment.

The number of portions is not allowed to increase indefinitely. The activity of the most soluble portion diminishes as the number increases. When its activity becomes inconsiderable, it is withdrawn from the fractionation. When the desired number of fractions has been obtained, fractionation of the least soluble portion is stopped (the richest in radium), and it is withdrawn from the remainder.

A fixed number of fractions is used in the process. After each series of operations, the saturated solution arising from one fraction is added to the crystals arising from the following fraction; but if after one of the series the most soluble fraction has been withdrawn, then, after the following series, a new fraction is made from the most soluble portion, and the crystals of the most active portion are withdrawn. By the successive alternation of these two processes, an extremely regular system of fractionation is obtained, in which the number of fractions and the activity of each remains constant, each being about five times as active as the subsequent one, and in which, on the one hand, an almost inactive product is removed, whilst, on the other, is obtained a chloride rich in radium. The amount of material contained in these fractions gradually diminishes, becoming less as the activity increases.

At first six fractions were used, and the activity of the chloride obtained at the end was only 0.1 that of uranium.

When most of the inactive matter has been removed, and the fractions have become small, one fraction is removed from the one end, and another is added to the other end consisting of the active chloride previously removed. A chloride richer in radium than the preceding is thus obtained. This system is continued until the crystals obtained are pure radium chloride. If the fractionation has been thoroughly carried out, scarcely any trace of the intermediate products remain.

At an advanced stage of the fractionation, when the quantity of material in each fraction is small, the separation by crystallisation is less efficacious, the cooling being too rapid and the volume of the solution to be decanted too small. It is then advisable to add water containing a known quantity of hydrochloric acid; this quantity may be increased as the fractionation proceeds.

The advantage gained thus consists in increasing the quantity of the solution, the solubility of the chlorides being less in water acidified with hydrochloric acid than in pure water. By using water containing much acid, excellent separations are effected, and it is only necessary to work with three or four fractions.

The crystals, which form in very acid solution, are elongated needles, those of barium chloride having exactly the same appearance as those of radium chloride. Both show double refraction. Crystals of barium chloride containing radium are colourless, but when the proportion of radium becomes greater, they have a yellow colouration after some hours, verging on orange, and sometimes a beautiful pink. This colour disappears in solution. Crystals of pure radium chloride are not coloured, so that the colouration appears to be due to the mixture of radium and barium. The maximum colouration is obtained for a certain degree of radium present, and this fact serves to check the progress of the fractionation.

I have sometimes noticed the formation of a deposit composed of crystals of which one part remained uncoloured, whilst the other was coloured, and it seems possible that the colourless crystals might be sorted out.

The fractional precipitation of an aqueous solution of barium chloride by alcohol also leads to the isolation of radium chloride, which is the first to precipitate. This method, which I first employed, was finally abandoned for the one just described, which proceeds with more regularity. I have, however, occasionally made use of precipitation by alcohol to purify radium chloride which contains traces of barium chloride. The latter remains in the slightly aqueous alcoholic solution, and can thus be removed.

M. Giesel, who, since the publication of our first researches, has been preparing radio-active bodies, recommends the separation of barium and radium by fractional crystallisation in water from a mixture of the bromides. I can testify that this method is advantageous, especially in the first stages of the fractionation.

(To be continued).

POINTS IN THE SYNTHESIS OF CAMPHOR AND OF INDIARUBBER.

By JOHN GEDDES McINTOSH.

THE crude product obtained by the action of hydrochloric acid on American spirits of turpentine, when distilled by my patent process over soda-ley, yields a small quantity of a residual substance which I believe to be identical with Bouchardat's so-called synthetic rubber from isoprene.

When the solid pinene mono-hydrochloride is distilled with zinc-dust, it is entirely converted into a liquid compound, the properties of which I am investigating. Unlike other distillates obtained by the use of various other reagents, this one is entirely free from chlorine.

Analytical Laboratory,
9, Parsonage Street, Cubitt Town, E.,
September 8, 1903.

CORRESPONDENCE.

RADIUM AND HELIUM.

To the Editor of the Chemical News.

SIR,—It appears from the work of Sir William Ramsay and Mr. Soddy that the radium emanation is actually producing helium (and, presumably, other bodies of the same class), the process being associated with the decay of the radio-activity of the emanation. This fact seems to establish a connection between valency and radio-activity—a view which has been previously expressed in your columns (*vide* CHEMICAL NEWS, 1901, lxxxiii., 130; 1902, lxxxv., 205 and 310). For it certainly looks as if a divalent element like radium, by the simple process of throwing off electrons (or valency bonds, on the Helmholtz theory of valence), is producing bodies of a non-valent nature.—I am, &c.,

GEOFFREY MARTIN.

Kiel, August 30, 1903.

PATENTS FOR INVENTIONS.

To the Editor of the Chemical News.

SIR,—It is probable that the majority of British inventors and patentees are aware of the introduction of an "Australian Federal Patents Bill" by the Commonwealth of Australia.

The Bill was presented and read on the 26th day of June last, and will probably become law in the Commonwealth by the beginning of next year.

The Bill contains one provision of such far-reaching consequence that we think too much prominence cannot be given to it. The provision we refer to is contained in Section 83, as follows:—

"Every patent shall be granted subject to the following conditions:—

- That the patentee or some person authorised by him shall within five years after the date thereof commence and after such commencement continuously carry on in Australia the construction manufacture or working of the invention patented in such a manner that any person desiring to use it may obtain it or the use of it at a reasonable price; and
- That the patentee shall not after four years from the date of the patent import the invention or cause it to be imported into Australia."

Thus it follows that an English manufacturer who obtains a patent for his product in the Australian Commonwealth must actually manufacture on the spot, and refrain from exporting the same from this country after a period of four years or lose his patent.

We also beg to draw your attention to the Canadian Patent Law which was amended by the Act of August 13, 1903, and which provides that the patentee or his representative must within two years commence and continuously carry on in Canada the construction or manufacture of his invention.

If, after the expiration of twelve months from the grant of a patent, the patentee or his representative imports into Canada the invention for which the patent is granted the patent shall be void.

These provisions are so widely different from the provisions in the mother country, and are likely to very seriously affect the position of British patentees, that no excuse is necessary for drawing your attention to the same.

—We are, &c.,
J. E. EVANS-JACKSON and Co.
Bristol House,
19 & 20, Holborn Viaduct, London, E.C.,
September 9, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 6, August 10, 1903.

Description of a New Apparatus for the Preparation of Pure Gases.—Henri Moissan.—The author describes an apparatus which overcomes a number of the difficulties associated with the preparation of pure gases, and using this prepares pure specimens of carbon dioxide, hydriodic acid, hydrochloric acid, hydrogen phosphide, sulphuretted hydrogen, and nitric oxide.

Certain Binary Compounds of Uranium.—A. Colani.—The author employs the double chloride of uranium and sodium, $\text{UCl}_2\cdot\text{NaCl}$, for the preparation of various uranium compounds. This substance has the advantage of being very slightly hygroscopic, and is scarcely more volatile than NaCl . He prepares in a pure state and investigates the properties of the sulphide, selenide, and telluride, nitride, phosphide, arsenide, and antimonide of uranium, and finds that the compounds of uranium with the trivalent metalloids burn with difficulty in air, but if thrown into the flame of a Bunsen burner cause brilliant sparks to appear. They are all violently attacked by concentrated nitric acid.

No. 7, August 17, 1903.

Properties of Nickel Steels.—Léon Guillet.—The author devises a diagram showing the properties of nickel steels. It contains four spaces; one corresponding to steels having the same structure as carbon steels, another to martensite with iron, a third to pure martensite, and the fourth to pure iron. The diagram also allows of the composition of the steels being deduced from its structure, and consequently its mechanical properties.

Disymmetric Tetramethyldiamino-Diphenylene-phenylmethane and the Colouring matter which is Derived from it.—A. Guyot and M. Granderye.—To prepare disymmetric tetramethyldiamino-diphenylene-phenylmethane the *o*-amine-derivative of the leucobose green malachite is dissolved in sulphuric acid, and treated with a solution of sodium nitrite, first at a low temperature, and finally at 100° to decompose the diazoic compounds. The yield under these conditions is about 16 per cent of the theoretical yield. The substance is then purified by being several times crystallised by precipitation from benzene by means of boiling alcohol in the form of fine white crystals melting at 149° , very soluble in benzene and very slightly soluble in alcohol.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Southport Meeting of the British Association:—

President—Prof. Walter Noel Hartley, D.Sc., F.R.S., F.R.S.E.

Vice-Presidents—Prof. J. Campbell Brown, D.Sc.; Prof. E. Divers, M.D., F.R.S.; Prof. F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Prof. Sydney Young, D.Sc., F.R.S.

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D.Sc., Ph.D.; Prof. James Dewar, F.R.S.; Prof. Harold B. Dixon, F.R.S.; Prof. J. J. Dobbie, D.Sc.; T. Fairley, F.I.C.; J. T. Hewitt, D.Sc., M.A.; Julius Hübner; Francis Jones, F.I.C.; C. A. Kohn, Ph.D.; Arthur R. Ling, F.I.C.; Prof. E. A. Letts, D.Sc.; M. Matsubara, Ph.D.; Hugh Marshall, D.Sc.; Prof. T. Purdie, F.R.S.; Hugh Ramage, M.A.; Sir Henry E. Roscoe, F.R.S.; Prof. A. Senior, Ph.D.; R. L. Taylor, F.I.C.; Prof. T. Turner, F.I.C.

The Papers brought before the Section were as follows:—

President's Address.

Prof. J. Campbell Brown—Apparatus for determining Latent Heat of Evaporation.

Miss Ida Smedley—On some Derivatives of Fluorene.

A. R. Ling—Action of Diastase on the Starch Granules of Raw and Malted Barley.

A. R. Ling—Action of Malt Diastase on Potato Starch Paste.

B. F. Davis and A. R. Ling—Action of Malt Diastase on Potato Starch Paste.

Dr. H. C. White—The Chemical and Physical Characteristics of the so-called Mad-stone.

Prof. E. A. Letts, R. F. Blake, and J. S. Totton—Reduction of Nitrates by Sewage.

R. L. Taylor—A Method for the Separation of Cobalt from Nickel, and the Volumetric Determination of Cobalt.

Dr. H. E. Armstrong—Report of Committee on Isomorphous Sulphonic Derivatives of Benzene.

Dr. H. E. Armstrong—Report of Committee on Isomeric Naphthalene Derivatives.

Dr. M. O. Forster—Report of Committee on the Possibility of making Special Reports more Available than at Present.

Sir Henry E. Roscoe—Report of the Committee on Duty Free Alcohol.

J. Hübner and Prof. W. J. Pope—The cause of the Lustre produced on Mercerising Cotton under Tension.

Prof. James Dewar—Investigations at Low Temperatures:—(a) Densities of Solid Hydrogen, Nitrogen, and Oxygen. (b) Methods of Producing Solid Hydrogen and Nitrogen. (c) Latent Heat, Specific Heat, and Coefficient of Expansion of Liquid Hydrogen.

Dr. A. Macfadyen—The Application of Low Temperatures to the Study of Biological Problems.

Prof. T. Turner—Stead's Recent Experiments on the Causes and Prevention of Brittleness in Steel.

W. Ackroyd—The Colour of Iodides.

Dr. O. Silberrad—On Essential Oils.

Dr. R. H. Pickard—The Cholesterol Group.

Prof. A. Senior—On Acridines.

M. le Comte A. de Gramont—Sur le Spectre de Self-induction du Silicium et ses Comparaisons Astronomiques.

Prof. G. von Georgiewics—The Theory of Dyeing.

Dr. W. A. Bone—The Slow Combustion of Methane and Ethane. (A discussion ensued on the General Subject of Combustion).

Dr. J. T. Hewitt—Fluorescence as Related to the Constitution of Organic Substances.

J. E. Petavel and R. S. Hutton—Preliminary Note on some Electric Furnace Reactions under High Gaseous Pressure.

Holland Crompton—The Atomic Latent Heats of Fusion of the Metals, considered from the Kinetic Standpoint.

Dr. E. Perman—The Influence of Small Quantities of Water in bringing about Chemical Reactions between Salts.

Prof. W. N. Hartley—Report of Committee on Absorption Spectra and Chemical Constitution of Organic Substances.

Dr. J. C. Philip—Freezing-point Curves of Binary Mixtures.

Prof. T. Purdie and J. C. Irvine—A Contribution to the Constitution of Disaccharides.

- Dr. E. F. Armstrong*—Mutarotation in Relation to the Lactonic Structure of Glucose.
W. Sloan Mills—Synthesis of Glucosides.
W. Sloan Mills—Preparation of Oximido-Compounds.
W. Sloan Mills—The Action of Oxides of Nitrogen on Oximido-Compounds.
W. Thomson—Further Investigation of Approximate Estimation of Minute Quantities of Arsenic in Food.
Dr. A. W. Crossley—Report of Committee on the Study of Hydro-aromatic Substances.
Dr. Marshall Watts—Report of Committee on Wavelength Tables of the Spectra of the Elements and Compounds.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1903, the Fresenius Chemical Laboratory was attended by thirty-seven Students. Of these, twenty-seven were from Germany, two from Austria, one from England, one from Luxemburg, one from Holland, one from Switzerland, one from France, one from Russia, one from Transvaal, and one from Japan. There were three Assistants in the Instruction Laboratory, and twenty-four in the Versuchsstationen (private laboratories). To the certified staff of teachers belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Winter Term begins on October 15. During the Summer Term, 1903, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

Tungsten, Molybdenum, Uranium, and Titanium.—A. Stavenhagen and E. Schuchard.—The authors have obtained, by means of aluminothermy, alloys of WCo, WMo, MoV, MoFe, MoSb, UFe, UCo, UMn, TiFe, TiCo, TiCu, PbW, PbMo, FeBa, CrCuWMo, TiWMo, MoUCrTi, and FeMnU. Titanium cannot be obtained in a state of purity under these conditions. The easily reducible oxides, like PbO, Bi₂O₃, ZnO, or HgO, when mixed with powdered aluminium, give rise to violent explosions. The experiments were carried out by mixing up the oxides with powdered aluminium moistened with alcohol in a crucible, and in the half-dried masses a few vent holes were pierced by means of a stirring-rod. After desiccation heat was applied either by means of electricity or by a flame, or even by smokeless gunpowder.—*Berichte*, vol. xxxv., p. 909.

Transformation of Hypochlorites into Chlorates.—F. Foerster.—In this research the method adopted was based on the following reaction: $\text{HOCl} + \text{H}_2\text{O}_2 = \text{HCl} + \text{H}_2\text{O} + \text{O}_2$, by means of which hypochlorite can be titrated in the presence of chlorate. The results of the experiments are as follows:—(a). The reaction $\text{Cl}_2 + \text{H}_2\text{O} + \text{NaOCl} = \text{NaCl} + 2\text{ClOH}$ does not take place, and no augmentation of the amount of active chlorine is observed under these conditions. (b). Quantitative estimations confirm the equation $\text{ClO} + 2\text{ClOH} = \text{ClO}_3 + 2\text{H} + 2\text{Cl}$ when we react with hypochlorous acid on a solution of hypochlorite. (c). The formation of the chlorate in solutions containing the same total hypochlorous Cl, but with a variable proportion of ClOH and ClONa.—It was observed that the concentration of the ClOH remained constant as long as any hypochlorite remained. The determination of the speed of the reaction showed that the transformation of the hypochlorite took place according to a mono-molecular reaction; the constant of the reaction for different concentrations of ClOH is proportional to the square of the concentration; dilution considerably increases the time necessary for the total disappearance of the hypochlorite. (d). The formation of the chlorate increases with the concentration of the NaCl; the neutral salts (NaNO₃, for example) act in the same manner. (e). Action of ClOH on the alkaline chlorides.

—Among the neutral salts, the chlorides have a greater action than the other salts; if with NaNO₃ or NaClO₃, a solution of ClOH undergoes a loss of 6 per cent, in the case of NaCl of the same molecular concentration the loss is 40 per cent. Finally, the author shows that the low alkalinity observed by W. von Tiesenholt on evaporating a solution of ClOH, treated with NaCl, is due to the hydrolysis of the hypochlorite formed according to the equation of equilibrium: $\text{NaOCl} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{ClOH}$.—*Journ. f. Prakt. Ch.*, vol. lxxiii., p. 141.

Determination of Sulphur in Steel.—B. F. Weston (*Iron Age*).—The evolution method gives results 0.005 to 0.025 per cent low in pig- and cast-iron. G. T. Doughty has advocated annealing the drillings for fifteen minutes. The author has applied this annealing also to steel drillings of basic open-hearth steel. Results with 12 samples showed a gain of 0.0005 to 0.004 per cent sulphur by the evolution method, when the samples had been annealed fifteen minutes over a blast-lamp in a covered porcelain crucible. The average gain was 0.003 per cent.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Cut Potatoes—Would some reader be good enough to inform me the best way to preserve cut potatoes without destroying the germinating properties of the tuber. I am told there is some chemical with which the cut parts of the potato could be dressed that would stop the bleeding or dry up the cut parts. I am anxious to cut out the eyes of a new variety (to reduce the weight) to send abroad by Parcels Post.—*AMATEUR*.

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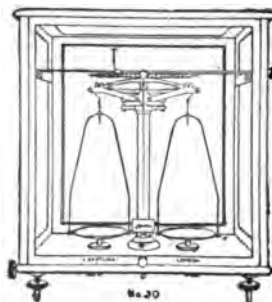
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VOL. LXXXVIII., No. 2287.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

SOUTHPORT, 1903.

By Professor W. N. HARTLEY, D.Sc., F.R.S., F.R.S.E.,
President of the Section.

(Concluded from p. 145).

ABSORPTION SPECTRA (*continued*).

Tautomerism.

THE possibility of an atom of hydrogen occupying alternative positions in a compound—



so that it may be united to an atom of nitrogen or of carbon in one instance, or to an atom of oxygen in another, easily gives rise to substances with different characters: the one that of a phenol, the other that of a ketone. One interpretation of the facts observed which has been very commonly received may be stated thus:—Certain compounds have in their constitution an atom of hydrogen of a "roving disposition" which at one time will attach itself to an atom of oxygen, or to an atom of nitrogen, and anon it will forsake one of these and unite itself to an atom of carbon. The consequence of this "instability of character" is that when a derivative of the compound is being prepared or sought for by a chemical process, which according to all previous knowledge ought to yield it, the substance brought forth is of a different class, but withal of the same composition; it is, in fact, an isomeride.

According to another theory, the two isomeric derivatives of the parent substance are present in equal proportions in a solution in a state of equilibrium, and upon crystallisation one or other of these assumes the solid form. Taking those cases where a substance has a constitution which it is believed has been correctly ascertained by chemical reactions, and which yields two isomeric alkyl derivatives, it becomes a question as to which of these the parent substance has directly given birth to. The evidence from chemical reactions has in many cases failed to give a satisfactory answer, but the curves of molecular vibrations of such substances afford the desired information concerning the relationship of their constitution to that of their respective derivatives.

Most convincing evidence has been afforded by observations on their spectra, that several of the parent substances are really not what they seem to be.

Thus, isatin and methyl pseudo-isatin yield curves which are almost identical, the sole difference between them being due to the substitution of the alkyl radical for hydrogen, the nature of which difference might have been predicted.

Clearly the parent substance and the pseudo-derivative are of the same nature and constitution.

Carbostyryl and methyl pseudo-carbostyryl, *o*-oxycarbanil and its ethyl ether, obtained by boiling with potash and ethyl iodide, are also similarly related, and they possess the ketonic or lactam structure.

On the other hand, methylisatin, carbostyryl, and the other ether of *o*-oxycarbanil yield curves which are essentially different from the foregoing, and are enolic or of the lactam type. Generally speaking, the ketonic are more stable than the enolic forms. Dibenzoyl methane is ketonic, and the tautomeric substance oxybenzal-acetophenone is enolic, and in this instance the enolic form is that with the greatest stability. The two substances

yield different curves, and the gradual change of the less stable into the more stable form can be traced by photographing the spectra of the solutions at intervals.

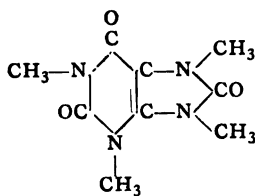
The ethyl esters of dibenzoyl succinic acid are of interest in this connection. There are three isomers known out of the thirteen which are possible, and the spectra of these have been studied. Knorr has given three formulæ for what he designates the α , β , and γ esters. Of these there are two, the β and γ forms, which give identical absorption curves: they are of the ketonic type, and structurally identical, but configuratively different, being stereo-isomerides.

The curve of molecular vibrations of the α ester is quite different from that common to the β and γ compounds. The α compound is of the enolic type, and it changes spontaneously at ordinary temperatures into the ketonic, thus showing that in this case also the latter is the more stable. The transition from the one form to the other was seen to be in progress, and after an interval of only three hours the absorption band of the enolic ester had almost entirely disappeared. In three weeks the transformation had become complete, as was shown by the molecular vibration curve of the α ester being almost exactly coincident with that of the β and γ forms.

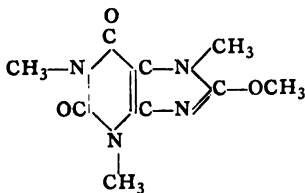
Another interesting example is afforded by the study of phloroglucinol, it being a substance with a constitution of a somewhat doubtful character, for owing to the ambiguity of its behaviour towards chemical reagents it is impossible to arrive at a decision from chemical evidence whether the oxygen atoms are present in enolic or ketonic groups. Towards some substances it behaves as a phenol, towards others as a ketone. The doubt also presented itself as to whether phloroglucinol from various sources had the same constitution, and, further, whether there might not be two isomeric forms of the compound present in equal proportions in a solution of the substance. Specimens of phloroglucinol prepared in five different ways from different materials gave curves of molecular vibrations which were identical: this decided the question absolutely; they are one and the same substance. If the constitution of the substance is that of a trihydroxybenzene or phenol, then the trimethyl ether should exhibit an absorption curve differing but slightly in detail from that of the parent substance; and, furthermore, the latter should exhibit a general resemblance to the curves of pyrogallol and phenol. This was found actually to be the case in both particulars.

Finally, with regard to tautomerism, it may be considered as decided that no evidence has been obtained based upon either physical measurements or chemical reactions of, first, the presence of a "wandering" atom of hydrogen as a characteristic of compounds which exhibit tautomerism; secondly, that solutions of tautomeric compounds do not contain equal quantities of the two substances, or enolic and ketonic forms in equilibrium, and that if both are present one so greatly preponderates over the other that no trace of any but the one compound can be detected; thirdly, it has been observed that some substances do change spontaneously from one form to another, and that this change sets in very quickly after the substance has been dissolved; fourthly, that substances change from one form to another under the influence of different reagents, as, for instance, cotarnine, as Dobbie and Lauder (1903) have shown, in presence of methyl alcohol or of caustic soda, and again in presence of potassium cyanide. In fact, it appears that, under the influence of different reagents, one or other of the two compounds is the more stable, and the more stable substance is then formed.

A reaction is recorded in the researches of Emil Fischer where it appears that two tautomeric forms are produced simultaneously from oxycafféine. When the silver salt of this substance is heated with methyl iodide it yields a mixture of tetramethyl uric acid and methoxycafféine, the characteristic groupings in which are —NH—CO— and —N=COH— , the hydrogens being methylated. This is a singular reaction which has not yet been studied spectrographically.



Tetramethyluric acid.



Methoxycaffeine.

The Absorption Spectra of Alkaloids.

The interest attached to an examination of the absorption spectra of the alkaloids is not alone the fact that a means of recognising, detecting, and estimating such substances was devised, but still more that we may learn something of their chemical constitution. Many of the poisonous alkaloids give no distinctive chemical reactions, and in certain cases the means of recognising them are restricted to observations on their crystalline form and their physiological action. The physiological action of certain alkaloids of an extremely deadly character is remarkable enough to prove a means of their identification when the effect on the human subject is under observation. The first experimental work on the absorption spectra of the alkaloids arose out of a celebrated trial for murder, which engaged much attention in the year 1882. It was proved that the lethal drug administered was aconitine.

To identify this substance, of which there are several varieties, it was necessary at that time to resort to physiological tests made upon small animals.

Such a course always affords an opportunity for forensic arguments based upon the evidence adduced. To substitute absolute physical measurements for physiological tests seemed to present facilities for securing justice by removing any doubt of the identity of an unknown substance with the nature of one which is known. Alkaloids yield spectra of two kinds, those which do not and those which do exhibit absorption bands, the difference between the two classes of substances being one dependent on the constitution of the nucleus or ultimate radical of the compound. It is possible not only to identify substances, but also to determine the quantity present in a mixture or solution, and this has actually been done.

Alkaloids which are derived from benzenoid hydrocarbons, pyridine, quinoline, or phenanthrene give evidence of their origin by their spectra. It is therefore advantageous to make a careful study of the absorption spectra of the substances themselves and of the various products derived from them when studying their constitution. It was remarked while the work was in progress that the quinine spectrum curve was probably due to the conjugation of four pyridine or two quinoline nuclei. It is known now to be a substance of a complicated structure containing one quinoline nucleus. It differs from cinchonine only by one methoxyl group in the *para*-position. Observations made on simple bases differ from those made on substitution products, such as alkyl derivatives, in this respect, that the bases are the more diastinct, while addition products, such as hydrogenised compounds, and also salts of the alkaloids, such as hydrochlorides, are more diastinct than the simple bases. It was shown by the researches of Alder Wright that different preparations of aconitine can yield substances slightly differing in constitution. On examining them it was shown that these preparations yielded different absorp-

tion curves, the variations in which were due to differences in the constitution of the different preparations. To state a particular case of a well-defined character, the aconitine from *Aconitum napellus* and japaconitine from a Japanese aconite prepared by Alder Wright had practically the same absorption spectrum and yielded similar curves; but that of japaconitine was just what might be expected from a substance with a nucleus of a similar constitution, but about twice the molecular weight of aconitine; in other words, a condensation of two molecules of aconitine into one—namely, what was observed in the spectra of morphine and apomorphine, a much greater absorptive power with a similar absorption curve.

It was shown that japaconitine has a constitution modified in such a manner; it being, in fact, what was termed by Alder Wright a sesquiapoaconitine; and the formulæ given for these substances are respectively:—Aconitine, $C_{34}H_{47}NO_{11}$; japaconitine, $C_{66}H_{88}N_2O_{21}$, which is in agreement with the spectrum observations. It has, however, been supposed by Freund and Beck that the two substances are identical.

Strychnine and brucine are two alkaloids evidently closely related, but little is known about their constitution; both seem to contain a pyridine nucleus united to what is probably a pyrrolic nucleus, the two constituting a conjugated nucleus resembling that of quinoline. The difference between brucine and strychnine is said to be simply that the former contains two methoxyls. The absorption curves show a wider difference than this, and it was predicted that strychnine appears to be a derivative of pyridine, but brucine is more probably a derivative of tetrahydroquinoline, or an addition product of quinoline of the same character, since there is a remarkable similarity between the curves of the two substances. I would suggest that for the future evidence from their spectra be taken into account in studying their constitution.

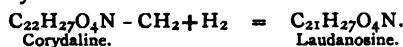
Stereoisomerism in the Alkaloids.

Many alkaloids having the same formula are stereoisomerides, and those related in this manner exhibit molecular absorption curves which are identical. The following examples are quoted by Dobbie and Lauder (1903) as the result of their investigations:—Dextro-corydaline and inactive corydaline; narcotine and gnoscopine; tetrahydroberberine and canadine. Where two compounds are known to have the same formula, and one of these is optically active, the other inactive, it may be inferred, as Dobbie and Lauder have pointed out, that they are not optical isomerides if their absorption curves are different; thus canadine and papaverine have the same formula, but their absorption curves show that they are structurally different.

It is a general rule that substances which agree closely in structure exhibit similar series of absorption spectra, while those which differ essentially in structure show absorption curves which are different; and to this rule neither aromatic compounds, alkaloids, nor dyes and coloured substances form any exceptions. That this is so is easily understood from the theory of absorption spectra. It must, however, be distinctly understood that the essential feature of importance in all such investigations is the quantitative relation of the substance to its spectra, whether these relations are based upon equal weights of material or equimolecular proportions in solutions of given volume and thickness.

The relationship of morphine, $C_{17}H_{17}NO(OH)_2$, and codeine or methylmorphine, $C_{17}H_{17}NO(OH)(OCH_3)$, was shown by their spectra, the latter being a homologue of the former. A similar instance has been investigated recently by Dobbie and Lauder. The resemblance between the spectra of laudanine, $C_{20}H_{25}O_4N$, and laudanoline, $C_{21}H_{27}O_4N$, confirms the view that they are homologous bases. The close agreement of their absorption curves with those of corydaline and tetrahydropapaverine clearly indicates a similarity in structure to that of these alkaloids, but the relationship of laudanoline to corydaline is probably

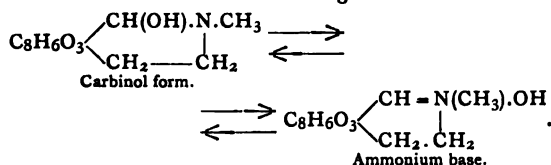
closer than to tetrahydropapaverine, and may be best explained by the formulæ—



The removal of a methyl group from such a compound would scarcely cause any appreciable change in the curve of molecular vibrations, and very many cases are known where, when two atoms of hydrogen are introduced into a compound without altering the close linking of the carbon atoms of the ring formation in the compound, the alteration in the spectrum is insignificant.

A particularly interesting example of tautomerism already mentioned has been observed by Dobbie and Lauder in studying the constitution of cotarnine, a substance prepared from narcotine. Three formulæ have been proposed for it: one represents it as an aromatic aldehyde in which one hydrogen is replaced by an open chain containing nitrogen; a second gives it the character of a carbinol base; while a third that of an ammonium base. It has been supposed that in solution it is a mixture of two or all three such substances in a state of equilibrium, but as to what is the formula to be assigned to solid cotarnine the data are insufficient to determine. There are, however, two different solutions of the substance obtainable; that in ether or chloroform is quite colourless, like the solid; but a solution in water or alcohol is yellow. From the molecular absorption spectra of these solutions and of certain derivatives with which they are compared, there is very distinct evidence that a solution in alcohol or water contains the ammonium base, while under the influence of sodium hydroxide it assumes the condition of the carbinol form. Moreover, the rate of transformation and the conditions which influence this isomeric change have been studied. It suffices here to state that a solution containing entirely the one form may be converted wholly into the other.

The two formulæ referred to are given below:—



EMISSION SPECTRA.

Spark Spectra and their Constitution.

As it became necessary to make accurate measurements of absorption spectra in the ultra-violet, the work of obtaining the wave-lengths of lines in twenty metallic spectra was undertaken. They were for the most part in a region which, except in the case of two or three elements, had not been previously explored. A small Rutherford grating was employed, combined with quartz lenses with a focal length of three feet. Experience had shown that it was advisable in describing these spectra to give measurements in hundredths of an inch of the positions of the lines on the published photographs of the prismatic spectra in the *Journal of the Chemical Society* (March, 1882), and to follow Lecoq de Boisbaudran by giving a description of the character of each of the lines. In this way they are easily identified, and the value of the measurements for practical purposes is greatly enhanced. Prior to the publication of the work (1882), in the prosecution of which Dr. Adeney was associated with me, Liveing and Dewar, who had been engaged on a similar investigation, but operating in a different manner, published an account of the spectra of the metals of the alkalis and alkaline earths, and subsequently the lines of iron, nickel, and cobalt. They showed a rhythmic grouping of the lines to be characteristic of the spectra of the alkali metals.

In connection with the prismatic spectra which were photographed some remarkable facts were noticed; for instance, the character of the lines belonging to different groups of elements was a noticeable feature, as well also

their disposition or arrangement, more particularly in the ultra-violet. Similarities in the visible spectra of zinc and cadmium, of calcium, strontium, and barium, and in those of the alkali metals had been observed by Mitscherlich, by Lecoq de Boisbaudran, and also by Ciamician. As to the grouping of the lines as observed on the photographs, it appeared that the spectra of well-defined groups of elements had characteristics in common which were different from those of other groups. For instance, the alkali metals differed from the alkali earth metals which appeared to form a group by themselves. Then in marked contrast to these simple spectra were those of iron, nickel, and cobalt, which though very complicated were seen to be much alike. Nearest to these but differing from them in certain respects were the palladium, gold, and platinum spectra.

It was observed how these elements with certain chemical and physical properties in common could be recognised as being relations owing to their family likeness when their spectra were photographed. Then it was remarked that the spectra of magnesium, zinc, and cadmium had distinctive characters in common; for instance, the individual lines in these spectra were marked by similar characteristics, such as a great extension of the strong lines above and below the points of the electrodes. This extension was increased with the atomic mass of the metal, and with the greater atomic mass in this group the volatility of the metal is also greater. An arrangement of the lines in pairs and triplets was noticed, the triplets being repeated, but less distinctly than in the first instance, and again repeated sharply but less strongly, so that there were three different sets of triplets in each spectrum. The point of greatest interest and importance was the connection traced between the atomic mass and the numerical differences observed in the intervals between the lines of different groups when measured by their oscillation frequencies.

These differences were not in the spectrum of one element, but were in the lines of each metal of the group, and were clearly associated with the atomic mass and chemical properties in each case.

The arrangement of the lines, which was common to all the metals in the magnesium, zinc, cadmium group, may shortly be described as follows:—Three isolated lines and one pair of lines in magnesium, with four sets of triplets; one isolated line and one pair of lines in zinc, with three sets of triplets; one isolated line and one pair of lines in cadmium, with three sets of triplets.

Besides the arrangement of these lines there were in the spectrum of each element two groups of the most refrangible lines, consisting one of a quadruple group and the other of a quintuple group, the groups and the lines composing them being similarly disposed in each spectrum. It was, however, not distinctly proved that these particular groups were strictly homologous, the most refrangible lines in the zinc spectrum being very difficult to photograph even on specially prepared plates, though the lines are strong. It was furthermore observed that with an increase in the atomic mass the distances between the lines, both in pairs and triplets, were greater. The same was the case with the quadruple and quintuple groups. In the magnesium spectrum, if we compare the first with the second group of triplets, we find the intervals extending from the first line in the first group to the first line in the second group, and from the second line in the first group to the second line in the second group, and from the third line in the first group to the third line in the second group, when measured in terms of oscillation frequencies, to be 677.1, 677.0, and 677.4. Similarly, taking the second and third groups, it is 391.2, 391.1, and 391.1. Between the third and fourth groups in like manner it is 230.9, 233, and 233; so that the intervals diminish with increase of refrangibility of the lines.

In the zinc spectrum the intervals between the lines in the first and second groups are 910, 910, and 910; in the second and third groups, 582, 581, and 583.

In the cadmium spectrum the corresponding intervals are 801·5, 800, and 800; in the second and third groups, 588, 589, and 587. The more accurately the lines are measured the more exactly do these differences correspond. It is scarcely necessary to point out that the differences in the atomic masses of the elements are in round numbers where $H=1$, $Mg\ 24$, $Zn\ 65$, and $Cd\ 112$.

The Law of Constant Differences rendered it evident that the spectra of the elements were subject to a law of homology, which was closely connected with the atomic mass and with their chemical and physical properties.

It was, in fact, found, in accordance with the periodic law, that the spectra of definite groups were spectra similarly constituted, from which it was deduced that they are produced by similarly constituted molecules. It is evident that there is periodicity in their spectra. The metals studied being all monatomic in their molecular condition, the conclusion was inevitable that the atoms were of complex constitution, and that not only was the complex nature of these atoms disclosed, but it was also shown that groups of elements with similar chemical and physical properties, the atomic weights of which differed by fixed definite values, were composed of the same kind of matter, but the matter of the different elements was in different states of condensation, as we know it to be in different members of the same homologous series of organic compounds. If this were not the case, the mass or quantity of matter in the atom would not affect in the same manner its rate of vibration—which the facts observed lead us to conclude that it does—and the chemical properties of the substances would differ more widely from one another, and the differences between them would not be gradational, which in fact they are. It was thus impossible to believe that the atoms were the ultimate particles of matter, though so far as chemical investigations had proceeded they were parts which had not been divided. Here the conviction was forced upon one that matter might exist in a state which had hitherto been unrecognised by those who accepted the atomic theory without searching beneath it. All that the atomic theory enabled the chemist to take account of were the laws of combination and decomposition of the forms of matter that are ponderable and of sufficient mass to be weighable on the finest balances, which are after all but crude and imperfect instruments for the study of matter, since they are capable only of determining differences between masses of tangible size. It became conceivable that matter in the state of gas or vapour might become so attenuated that repulsion of the molecules would be greater than the attraction; that they would then no longer form aggregates, and in consequence would cease to be weighable. In such a condition they may be imagined to constitute the ether, and in view of this conception there may be recognised four physical conditions of material substances, namely, solid, liquid, gas, and ether.

It is more than twenty years ago since the study of homology in spectra led me to the conviction that the chemical atoms are not the ultimate particles of matter, and that they have a complex constitution.

That the atoms of definite groups of chemically related elements are composed of the same kind of matter in different states of condensation is not a dream or a view of a visionary character, for it is based upon definite observations controlled by exact physical measurements, and is therefore in the nature of a theory rather than an hypothesis. Batchinski (1903) regards the atoms as being in a state of vibration, and the periods of vibration of related elements appear to stand in a simple relation to their properties. The mass of an atom is proportional to the square of its period of vibration, and conversely the vibration period of the atom may be calculated from the square root of the atomic weight. These values have been calculated and arranged according to Mendeleeff's classification, whereby it is shown that there is a decided tendency to form harmonic series in the vertical columns. The deviations are probably capable of explanation, as the author believes, on the ground that the atom is not to be

regarded as a material point, but as a material system. It is well to remember that the precursor of the Periodic Law was Newlands' Law of Octaves.

I have always experienced great difficulty in accepting the view that because the spectrum of an element contained a line or lines in it which were coincident with a line or lines in another element it was evidence of the dissociation of the elements into simpler forms of matter. In my opinion, evidence of the compound nature of the elements has never been obtained from the coincidence of a line or lines exclusively belonging to the spectrum of one element with a line or lines in the spectrum exclusively belonging to another element. This view is based upon the following grounds:—First, because the coincidences have generally been shown to be only apparent, and have never been proved to be real; secondly, because the great difficulty of obtaining one kind of matter entirely free from every other kind of matter is so great that where coincident lines occur in the spectra of what have been believed to be elementary substances, they have been shown from time to time to be caused by traces of foreign matter, such as by chemists are commonly termed impurities; thirdly, no instance has ever been recorded of any homologous group of lines belonging to one element occurring in the spectrum of another, except and alone where the one has been shown to constitute an impurity in the other; as, for instance, where the triplet of zinc is found in cadmium and the triplet of cadmium in zinc; the three strongest lines in the quintuple group of magnesium is graphite, and so on. The latest elucidation of the cause of coincidences of this kind arises out of a tabulated record from the wave-length measurements of about three thousand lines in the spectra of sixteen elements made by Adeney and myself. The instances where lines appeared to coincide were extremely rare; but there was one remarkable case of a group of lines in the spectrum of copper which appeared to be common to tellurium; also lines in indium, tin, antimony, and bismuth which seemed to have an origin in common with those of tellurium.

It is difficult to separate tellurium from copper, and copper from tellurium, by ordinary chemical processes. Dr. Köthner, of Charlottenburg, has succeeded in obtaining very pure tellurium from the spectrum of which these lines and also several others have been almost entirely eliminated, which shows that they are foreign to the element, and that his specimen of tellurium is probably purer than any previously obtained. For determining the atomic weight of tellurium it is of course necessary to obtain it in the greatest possible state of purity; and it may be mentioned that the material which Staudenmaier employed for this purpose was found, from Köthner's photograph of its spectrum, to be a very pure specimen.

The prosecution of researches in connection with the constitution of spectra was initiated by Johnstone Stoney, by Balmer with respect to hydrogen, and continued by Rydberg, Deslandres, Ames, and, above all, by Kayser and Runge, who by an elaborate and exhaustive investigation of the arc spectra of the elements have given us formulæ by which the wave-lengths of lines in the spectra of different elements in certain definite groups may be calculated. They also showed the spectra to be constituted of three series of lines, the principal series and two subordinate series, one sharp and the other diffuse.

Ramage, however, has given us a simpler formula depending on the atomic weight which applies to several groups, and he has co-ordinated the spectra of several of the elements with the squares of their atomic masses, and also their atomic masses with others of their physical properties.

It may here be remarked that the homology of the spark spectra in the magnesium, zinc, and cadmium series was at first called in question by Ames, though he proved the arc spectra of zinc and cadmium to be strictly homologous.

Preston decided the question by demonstrating by means of beautiful photographs that corresponding lines such as the pairs, triplets, and the quadruple groups in the

spark spectra of the three metals when under the influence of a very powerful magnetic field underwent the same kind of change; for instance, each quadruple group changed to sextuple, the second and fourth lines in each group becoming double. Lines in spectra which have not the same constitution behave differently. Recently, Runge and Paschen have arrived at the same conclusion; and, furthermore, have established homology in the spectra of sodium, copper, and silver; also between aluminium and thallium. Indium is almost certainly homologous with aluminium and thallium, but it was probably not investigated on account of its rarity. Marshall Watts has pointed out that a relationship exists between the lines in the spectra of some elements and the squares of their atomic weights, from which it is possible to calculate the atomic weight of an element if that of another in the same homologous series is known, and the oscillation frequencies of corresponding lines are known.

The knowledge of spectra we now possess enables the determination of atomic weights to be controlled with quite as much efficiency and certainty in many instances as by specific heat or vapour-density determinations.

The first application of the observed homology in spectra was directed towards the question of the atomic mass of beryllium, for which purpose the lines in the ultra-violet spark spectrum of this element were first photographed and measured. The nature of the evidence on the subject adduced at the time was in outline as follows:—

"If, as Nilson and Petterson suggest, the position of beryllium is at the head of a series of triad rare earth metals, the element scandium (at. wt. 44) and yttrium (at. wt. 89) must be members of the same group. If this be the case the spectra of the three elements must have certain characters in common, for the series of which aluminium and indium are the first and third terms yield strictly homologous spectra. As a matter of fact, no two spectra could be more dissimilar than those of beryllium and scandium."

Having compared the photographs and wave-length measurements of a large number of spectra of the elements, I felt justified in making the following remarks:—

"The spectrum of beryllium exhibits no marked analogy with the calcium, the magnesium, or the aluminium spectra, all of which are members of well-defined homologous series. There is nothing similar in it to the boron, silicon, or carbon spectra, nor to those of the scandium, yttrium, or cerium. The spectrum of lithium is most closely analogous to that of beryllium in the number, relative positions, and intensities of the lines. This leads to the conclusion that beryllium is the first member of a dyad series of metals, to which in all probability calcium, strontium, and barium, as a sub-group, are homologous, its atomic mass being 9.2, its place is above magnesium." Subsequently, Nilson, and also Humpidge, by chemical evidence and from vapour-density determinations of certain compounds, substantiated the conclusion previously arrived at by Emerson Reynolds, that the atomic mass of beryllium was not 13.8 but 9.2.

The next practical application of the spark spectra was to the analysis of rhabdophane, a mineral found many years ago in Cornwall, and described by Heuland in 1837 as a zinc blende of a peculiar character.

This mineral I found to contain neither zinc nor sulphur, and therefore it is not a blende. It is, in fact, a phosphate of the formula $R_2O_3 \cdot P_2O_5 \cdot 2H_2O$, in which the oxides of cerium, didymium, lanthanum, and yttrium may wholly or in part replace each other. The didymium absorption spectrum is well seen both by reflection from the surface and transmission through thin sections of the mineral. The spark spectrum of the yttrium chloride obtained from rhabdophane was compared with that observed by Thalen and ascribed to yttrium. Of the fifty-one lines in the spectrum of yttrium thirty-eight were absent from the yttrium obtained from rhabdophane, and it was concluded that the purest yttrium was that which yielded the simplest spectrum. This was the first occasion of the finding of

yttrium in any British mineral. Quite recently a confirmation of this view has been obtained by comparing this spectrum with lists of the arc lines of yttrium and ytterbium which have just been published by Kayser (1903).

Penfield analysed a mineral found in the United States which he named scovellite; it proved to be identical in species with rhabdophane.

Flame Spectra at High Temperatures.

What are commonly known in the chemical laboratory as flame spectra are chiefly those of the metals of the alkalis and alkaline earths; also of gallium, indium, and thallium. The researches of Mitscherlich and Lecoq de Boisbaudran first showed that copper, manganese, and gold gave flame spectra. Lockyer, Gouy, and Marshall Watts also investigated flame spectra.

In 1887 I used iridium wires one millimetre thick, twisted into loops upon which fragments of minerals were heated in the oxygen blowpipe flame. Natural silicates yielded spectra not only of alkalis but of the alkaline earths, and also distinct manganese spectra. Bartya, strontia, and lime gave spectra when insoluble compounds such as the sulphates were thus examined at high temperatures. Iron, cobalt, and nickel gave spectra even when compounds such as the oxides were heated strongly. But iridium, though infusible, is somewhat volatile, and contributes a line spectrum to the flame. In 1890 thin slips of the mineral kyanite and even pieces of tobacco pipe were used instead. Experience with this method of working went to show how the flame spectra of oxides of calcium, strontium, and barium could be separated from those of lithium, sodium, potassium, rubidium, and caesium, as observed in the Bunsen flame. Furthermore, that even the most volatile of these substances could be made to yield a continuous colouration from a single bead of salt for a period exceeding fifteen minutes, and extending to one or two hours, so that measurements of the lines might be made with some degree of certainty.

In order to study the flames emitted from furnaces during metallurgical operations, and particularly from the mouth of Bessemer vessels, it became necessary to ascertain what really were the lines of the elements observed under different conditions at a high temperature, and accordingly systematic methods of study were developed from the previous somewhat tentative experiments.

In all the flame spectra obtained by the oxyhydrogen blowpipe the ultra-violet line spectrum emitted by water-vapour which had been discovered by Huggins and by Liveing and Dewar was visible on the photographs by reason of the combustion of the hydrogen in the hydrocarbon, or the hydrogen gas itself, when burnt along with oxygen. The flame spectra are always shorter than those obtained from the arc or from condensed sparks. After an extended examination of spectra produced by the oxyhydrogen blowpipe from solid substances, the knowledge obtained was applied to the examination of the flames coming from the Bessemer vessel during the "blow" during all periods from the commencement to the termination. These observations were made at the London and North-Western Railway Steel Works at Crewe; and at Dowlais, in South Wales. In collaboration with Mr. Ramage, a large number of these complicated spectra were photographed at the North-Eastern Steel Works, where the Thomas-Gilchrist process is carried out. The spectra were fully described and measured, with the result that every one of the lines and bands was accounted for. A new line belonging to potassium was discovered to have peculiar properties. Gallium was proved to be present in the Cleveland ore from Yorkshire, in the finished metal, in clays and in all aluminous minerals, even in corundum. Also, by very accurate determinations of the wave-lengths of its principal lines, gallium was proved to be a constituent of the sun. Moreover, it was found in several meteorites. Pure gallium oxide was separated, by analytical methods, from iron ores and other materials; and the proportion of the metal in the steel rails made by the North-Eastern

Steel Company, of Middlesbrough, was determined and found to be one part in thirty thousand. This Yorkshire steel is richer in gallium than any other substance from which it has been extracted; for instance, the Bensburg blende, supposed hitherto to be the richest ore, contains only one part in fifty thousand.

By observations on the spectra, the thermo-chemistry of the Bessemer process of steel manufacture was studied, and the temperatures attained under varying conditions were estimated. The demonstration of the great volatility of most metals, and of many metallic oxides in an undecomposed condition, at the temperature of the oxyhydrogen blowpipe and of the Bessemer flame, was of special interest. The metals chiefly referred to are copper, silver, lead, tin, manganese, chromium, iron, cobalt, nickel, palladium, gold, and iridium. Several of these, such as silver and gold, have lately been distilled *in vacuo* by Kraft.

Banded Flame Spectra.

Well-defined groups of elements yield banded flame spectra which have a similar constitution; thus magnesium, zinc, and cadmium yield bands composed of fine lines, degraded towards the violet, while fluted band spectra of beryllium, aluminium, and indium were found to be degraded towards the red. Thallium also yields a fluted spectrum; gallium gives a line spectrum; lanthanum gives bands degraded towards the red; palladium gives bands in the nature of flutings composed of fine lines; germanium gave very faint indications of bands; rhodium and iridium both lines and bands. It became manifest that elements belonging to the same group in the periodic system of classification exhibited banded spectra which are similarly constituted, and hence similarly constituted molecules of the elements have similar modes of vibration, whether at the lower temperature of the flame or at the higher temperature of the arc or spark. Banded spectra are thus shown to be connected with the periodic law.

A great advantage is to be derived from an investigation of banded spectra from a theoretical point of view, as well as from the application of this method to the analysis of terrestrial matter. While the spectra are easily obtained, they can be applied in a very simple manner to the chemical analysis of minute quantities of material, and may readily be made quantitative.

M. Armand de Gramont has described a method of obtaining spectra of metals and metalloids by means of a spark, and has given the analysis of eighty-six mineral species. The novelty and importance of his work lies in the method of obtaining spectra of such constituent substances as chlorine, bromine and iodine, sulphur, selenium, and tellurium; also phosphorus and carbon when in a state of combination, as sulphates, phosphates, carbonates, &c.

There is a possibility of utilising this method for the quantitative determination of carbon, sulphur, and phosphorus in iron and steel during the process of manufacture.

Definition of an Element.

In a discussion on the question of the elementary character of argon in 1895, it was pointed out by me that argon gave a distinct spark spectrum by the action of condensed sparks, and therefore, on this evidence alone, it must be regarded as an element. The fact that it gave two spectra under different conditions was not opposed to, nor did it invalidate, this evidence, because such an element as nitrogen not only emits two spark spectra, but the two spectra can be readily photographed simultaneously from the same spark discharge.

It was proposed by M. de Gramont, at the International Congress in Paris in 1900, and agreed, that no new substance should be described as an element until its spark spectrum had been measured and shown to be different from that of every other known form of matter.

This appears to me to have been one of the most important transactions of the Congress. The first application of this rule has resulted in the recognition of radium as a new element; it is characterised by a special spark

spectrum of fifteen lines which have been fully studied and measured by Demarçay. It shows no lines of any other element.

Another application of this rule has recently been made by Exner and Haschek with preparations of the oxide of an element obtained by Demarçay, and named europium. It exhibits 1193 spark lines and 257 arc lines.

I have already mentioned that one feature strikingly shown in the spectra of chemically related elements was the wider separation of the lines in pairs, triplets, or other groups; was in some way related to the atomic mass, since the separation was greater in those elements whose atomic weights were greater. Kayser and Runge, and also Rydberg, have shown that in the series of alkali metals the differences between the oscillation frequencies of the lines are very nearly proportional to the squares of the atomic weights. Runge and Precht have recently shown that in every group of elements that are chemically related, the atomic weight is proportional to some power of the distance separating the two lines of the pairs of which the spectrum is constituted. In other words, if the logarithms of the atomic weight and distance between the lines be taken as coordinates, the corresponding points of a group of elements which are chemically related will lie on a straight line. Applying this law to the determination of the atomic weight of radium, they find that the strongest lines of the new element are exactly analogous to the strongest barium lines, and to those of the closely related elements, magnesium, calcium, and strontium. The intervals between the two lines of each pair in the principal series, and in the first and second subordinate series, if measured on the scale of oscillation frequencies, are equal for each element, and the same law holds good for the spectrum of radium. From this the value 257.8 was found for the atomic mass of the element. This does not quite accord with the number obtained by Madame Curie, who found it to be 225. It will be interesting to see which number will eventually be proved to be the more correct.

It is now many years since I first pointed out that the absolute wave-lengths of the lines of emission spectra of the elements are physical constants of quite as great importance in theoretical chemistry as the atomic weights; in the light of recent discoveries this statement may be said to be now fully justified.

Radio-active Elements.

From the study of rays of measurable wave-lengths we have lately sailed under the guidance of M. Henri Becquerel into another region where it is doubtful whether all the rays conform to the undulatory theory. In fact, some of the rays are believed to be charged particles of matter, charged, that is to say, with electricity. Beyond doubt they are possessed of very extraordinary properties, inasmuch as they are able to penetrate the clothing, celluloid, gutta-percha, glass, and various metals. They are, moreover, endowed with a no less remarkable physiological action, producing blisters and ulcerations in the flesh which are difficult to heal. It is an established fact that such effects have been caused by only a few centigrams. of a radium compound contained in a glass tube enclosed in a thin metallic box carried in the pocket.

From this we can quite understand that there is no exaggeration in the statement attributed to the discoverer, Professor Curie, by Mr. W. J. Hanmer, of the American Institute of Electrical Engineers, that he would not care to trust himself in a room with a kilogram. of pure radium, because it would doubtless destroy his eyesight, burn all the skin off his body, and probably kill him.

It remains for me to express regret that without an undue extension of the time devoted to this address, it would have been scarcely possible to afford adequate treatment to the absorption spectra of inorganic compounds, particularly those of the rare earths, and such also as afford evidence of the chemical constitution of saline solutions; or of organic compounds closely related to coloured substances and dyes, the investigation of which leads to the elucidation

tion of the origin of colour, and serves to indicate the nature of the chemical reactions by which coloured substances may be evolved from those which are colourless.

Chemistry is popularly known as a science of far-reaching importance to specific arts, industries, and manufactures; but it occupies a peculiar position in this respect, that it is at one and the same time an abstract science, and one with an ever-increasing number of practical applications. To draw a line between the two, and say where the one ends and the other begins is impossible, because the theoretical problem of to-day may reappear upon the morrow as the foundation of a valuable invention.

ADDRESS TO THE
MATHEMATICAL AND PHYSICAL SECTION
OF THE
BRITISH ASSOCIATION.
SOUTHPORT, 1903.

By CHARLES VERNON BOYS, F.R.S.,
President of the Section.

THE first duty of every occupant of this Chair is a sad one. Year by year the record grows of those who have devoted their lives to the development of mathematical and physical science, of those who have completed their work. The past year has added many names to the record—more, it seems, than its fair share. The names include some of the most brilliant and active of our race, of those to whom this Association is deeply indebted, and also of our fellow workmen in other countries whose loss is no less to be deplored.

Lord Salisbury's devotion to the empire, of which this is not the occasion to speak, left him but little time for those scientific pursuits in which he took so keen an interest. Once, however, as President of this Association, he showed our members that, unlike the majority of our statesmen, science was not to him a phantom. His Address at Oxford will remain in the memories of all who heard it. The eloquence, the humour, the satire, the subtilty provided an intellectual treat of the rarest kind.

Of Sir George Gabriel Stokes and his work it is not possible for me to speak. Any attempt on my part to appreciate or gauge the value of the work of such a giant would be an impertinence. This can only fitly be done by one of our leaders, and Lord Kelvin has paid a fitting tribute in the pages of *Nature*. I can only record the fact that Stokes was for seven years Secretary, and twice President of this Section, and in 1869 was President of the Association.

Dr. Gladstone, for fifty-three years a member of this Association, was not only an unfailing attendant at our meetings, but an active member whose steady stream of original communications on subjects connecting physics and chemistry earned for him the designation of Creator of Physical Chemistry. His investigations on spectroscopy, refractivity, and electrolytics are known to every student of physics. His researches upon early metallurgical history, while of less importance to the progress of science, are none the less interesting. An ardent apostle of education, he was for twenty-one years a member of the London School Board, and three years Vice-Chairman. Dr. Gladstone was the first President of the Physical Society. He has been President of the Chemical Society, and at the last meeting of the British Association at Southport—as also in 1872—he was President of the Chemical Section. So long ago, he said, in urging the importance of science as a factor in education, that the so-called educated classes were not only ignorant of science, but had not arrived at the knowledge of their own ignorance.

It is not possible to pass on without paying a tribute, in which all who knew Dr. Gladstone will share, to his character no less than to his genius.

Sir William Roberts-Austen was probably one of the

most active members that this Association has known. Not only had he for many years made the subject of metals and alloys his own, but he worked for the Association in many ways. At three meetings have audiences been charmed by his fascinating and brilliant evening lectures, all relating to metals. He was President of the Chemical Section at the Cardiff meeting in 1891, and not only did he perform these duties, but he accepted the more laborious and more thankless task, for which his unfailing courtesy and tact so well fitted him, of acting as our General Secretary for four years. His labours in the important field of research which he tillied were appreciated by numerous technical societies and institutions of which he was an honorary member, or had been president or vice-president. Many branches of the public service had the advantage of his skill and experience, which received the official reward in 1899.

Dr. Common's skill as a designer and constructor of instruments was well known. His instinct or judgment in producing planes and figured concave mirrors of great dimensions was rare, for this is an art almost unknown in the laboratory. His generosity and his valuable advice have been appreciated by many besides myself.

Rev. H. W. Watson, Second Wrangler and Smith's Prizeman in 1850, was a Vice-President of the British Association in 1886. Mathematical physicists are familiar with the joint work of himself and Burbury on "Generalised Co-ordinates," and with his mathematical articles.

In Otto Hilger, the brother of the late Adam Hilger, who between them brought to this country German thoroughness and French skill in instrument manufacture, we have lost one of our first and most valuable constructors. Noted for the high class of all the optical work turned out by the firm, Otto Hilger was not afraid of attacking the problem of manufacturing the Michelson echelon grating. This little bundle of glass plates requires for its success perfection and precision commensurable only with the genius of the inventor. This Otto Hilger supplied.

Dean Farrar, a life member of the British Association, whose activity lay in another direction, showed his appreciation of the value of science in education by appointing the first science master at Marlborough when he became headmaster in the year 1870. As I was a boy at the school at that time, I can speak of the incredulity with which such an announcement was at first received, and of the general feeling that such an action was akin to a joke. I was, however, by no means the only boy who hailed the news with delight. We devoured the feast of chemistry and physics put before us by Rodwell and the books which at once became available. Out of gratitude to the late Dean of Canterbury I recall this episode.

James Wimshurst, the inventor of the influence machine which has carried his name into every corner of the scientific world, was not a member of this Association, but he fostered and encouraged the scientific spirit in young men who, by good fortune, came to know him. I do not think I have heard anyone spoken of with such gratitude and appreciation as Wimshurst, by men who in their younger days were allowed the run of his well-equipped workshop.

James Glaisher, best known as a balloonist in the sixties, has died at the great age of ninety-three. The balloon ascent with Coxwell on September 5, 1862, when they attained the altitude of 37,000 feet, will long remain in the popular imagination, not on account simply of the great altitude, but by reason of the sensational account of their having been paralysed with cold, and of their being able to stop the ever-increasing ascent only by the presence of mind of Coxwell, who, with his limbs frozen, seized the valve rope with his teeth, and so let out the gas.

While this event remains in everyone's mind, the more prosaic work of Glaisher in astronomy, meteorology, and photography, when most of us were children, and many yet unborn, led to his being elected president of various learned societies.

He gave one of the evening lectures of the British Association in 1863, the subject being balloon ascents.

A. F. Osler, the inventor of the self-recording direction and pressure anemometer and rain gauge, whose active meteorological work was carried out in the first half of the last century, when he contributed papers to the British Association and the Literary and Philosophical Society of Birmingham, has died at the still greater age of ninety-five. He was Vice-President of the British Association in 1865.

Of other countries, America has lost Professor J. Willard Gibbs, a mathematical physicist whose very learned and original contributions to the knowledge of the world on the thermodynamical properties of bodies, on vectors, the kinetic theory of gases, and other abstruse subjects, have received the highest recognition that the learned societies of this country can bestow. Professor Harkness, the astronomer, and Professor Rood, the skilled experimental physicist of Troy, have also maintained the high standard that we now look for in American science.

Germany has lost Professor Deichmüller, Professor of Astronomy at Bonn, at an early age. Sweden has lost Professor Bjerknes, whose hydrodynamical experiments showing attraction and repulsion were so much admired when he performed them at a meeting of the Physical Society some twenty-five years ago. Switzerland has lost Professor C. Dufour, the astronomer; and Italy has lost Professor Luigi Cremona, a foreign member of this Association, Principal of the Engineering School in Rome, whose contributions to pure geometry and to its applications have made him famous.

Of the events of the last year, one stands out beyond all others, not only for its intrinsic importance and revolutionary possibilities, but for the excitement that it has raised among the general public. The discovery by Professor and Madame Curie of what seems to be the everlasting production of heat in easily measurable quantity by a minute amount of a radium compound is so amazing that, even now that many of us have had the opportunity of seeing with our own eyes the heated thermometer, we hardly are able to believe what we see. This, which can barely be distinguished from the discovery of perpetual motion, which it is an axiom of science to call impossible, has left every chemist and physicist in a state of bewilderment. Added to this, Sir William Crookes has devised an experiment, characteristic of him, if I may say so, in which a particle of radium keeps a screen bombarded for ever, so it seems, each collision producing a microscopic flash of light, the dancing and multitude of which forcibly compel the imagination to follow the reasoning faculties, and realise the existence of atomic tumult. Thanks to the industry and genius of J. J. Thomson, Rutherford and Soddy, Sir William and Lady Huggins, Dewar and Ramsay, and others in this country, besides Professor and Madame Curie and a host of others abroad, this mystery is being attacked, and theories are being invented to account for the marvellous results of observation; but the theories themselves would a few years ago have seemed more wonderful and incredible than the facts, as we believe them to be, do to-day. An atom of radium can constantly produce an emanation, that is something like a gas, which escapes and carries with it wonderful properties; but the atom, the thing which cannot be divided, remains, and retains its weight. The emanation is truly wonderful. It is self-luminous, it is condensed by extreme cold, and vapourises again; it can be watched as it oozes through stop-cocks or hurries through tubes, but in amount it is so small that it has not yet been weighed. Sir William Ramsay has treated it with a chemical cruelty that would well-nigh have annihilated the most refractory or permanent known element; but this evanescent emanation comes out of the ordeal undimmed and undiminished.

Not content with manufacturing so remarkable a substance, the radium atom sends out three kinds of rays, one kind being much the same as Röntgen rays, but wholly different in ionising power, according to the experiments of Strutt. Each of these consists of particles which are shot out, but they have different penetrative power; they are differently deflected by magnets and also by electricity, and

the quantity of electricity in relation to the weight is different, and yet the atom, the same atom, remains unchanged and unchangeable. Not only this, but radium or its emanations or its rays must gradually create other bodies different from radium, and thus, so we are told, one at least of those new gases which but yesterday were discovered has its origin.

Then, again, just as these gases have no chemical properties, so the radium which produces them in some respects behaves in a manner contrary to that of all proper chemicals. It does not lose its power of creating heat even at the extreme cold of liquid air, while at the greater degree of cold of liquid hydrogen its activity is found by Professor Dewar to be actually greater.

Unlike old-fashioned chemicals which, when they are formed, have all their properties properly developed, radium and its salts take a month before they have acquired their full power (so Dewar tells us), and then, for anything we know to the contrary, proceed to manufacture heat, emanations, three kinds of rays, electricity, and gases for ever. For ever; well, perhaps not for ever, but for so long a time that the loss of weight in a year calculated, I suppose, rather than observed, is next to nothing. Professor Rutherford believes that thorium or uranium, which act in the same kind of way, but with far less vigour, would last a million years before there was nothing left, or at least before they were worn out; while the radium, preferring a short life and a merry one, could not expect to exist for more than a few thousand years.

In this time 1 grm. of radium would evolve one thousand million heat units, sufficient, if converted into work, to raise five hundred tons a mile high; whereas a grm. of hydrogen, our best fuel, burned in oxygen, only yields thirty-four thousand heat units, or one thirty-thousandth part of the output of radium. I believe that this is no exaggeration of what we are told and of what is believed to be experimentally proved with regard to radium; but if the half of it is true the term "the mystery of radium" is inadequate: the miracle of radium is the only expression that can be employed.

With all this mystery before us, which I must confess myself wholly unable to follow, I feel sure that members of the Association who are interested in the work of this Section will welcome the discussion, for which our secretaries have been able to arrange, and hear from the lips of Professor Rutherford the conclusions to which his researches have at present brought him. No one is more fitted than Professor Rutherford to open such a discussion, for no one has attacked the theoretical side with such originality and daring, or with such ingenuity of experiment.

As an example of the activity of mind and of research to which the activity of radium has given rise, I may mention the fact that the last number of the *Proceedings of the Royal Society* is wholly concerned with radium, there being four papers, all of the first importance, dealing with entirely different phenomena.

It is not my purpose to review these or the subject of radium generally; I am in no way fitted to do so. But I cannot well let the present opportunity pass of referring to another mystery of which a conspicuous example is now leaving us. I refer to the mystery of the comet and its tails. What is a comet? of what does its tails consist? Gravitational astronomy has told us for many years past that compared with the planets or their satellites a comet does not weigh anything. It weighs pounds or perhaps hundreds, thousands, or millions of tons; but in comparison with inconspicuous satellites it weighs nothing. Yet some of them as they approach the sun from remote regions begin to shoot out streamers which pour away as though repelled by the sun, not being left as a trail behind the comet, as is so often supposed. These streamers, ejected towards the sun, bend round and pour away at speeds which are enormous compared with that of the comet itself, thus producing the tail. Now these streams separate very often, and give rise to comets with two or three tails. Let me

read one paragraph from "The History of Astronomy," by Miss Clerke:—

"The amount of tail curvature, he (Olbers) pointed out, depends in each case upon the proportion borne by the velocity of the ascending particles to that of the comet in its orbit; the swifter the outrush the straighter the approaching tail. But the velocity of the ascending particles varies with the energy of their repulsion by the sun, and this again, it may be presumed, by their quality. Thus multiple tails are developed when the same comet throws off, as it approaches perihelion, specifically distinct substances. The long straight ray which proceeded from the comet of 1807, for example, was doubtless made up of particles subject to a much more vigorous solar repulsion than those formed into the shorter curved emanation issuing from it nearly in the same direction. In the comet of 1811 he calculated that the particles expelled from the head travelled to the remote extremity of the tail in eleven minutes, indicating by this enormous rapidity of movement (comparable to that of the transmission of light) the action of a force much more powerful than the opposing one of gravity. The not uncommon phenomena of multiple envelopes, on the other hand, he explained, are due to the varying amounts of repulsion exercised by the nucleus itself on the different kinds of matter developed from it.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 147).

CHAPTER II. (continued).

Determination of the Atomic Weight of Radium.

In the course of my work I determined at intervals the atomic weight of the metal contained in specimens of barium chloride containing radium. With each newly obtained product I carried the concentration as far as possible, so as to have from 0.1 grm. to 0.5 grm. of material containing most of the activity of the mixture. From this small quantity I precipitated with alcohol or with hydrochloric acid some milligrams of chloride for spectral analysis. Thanks to his excellent method, Demarcay only required this small quantity of material to obtain the photograph of the spark spectrum. I made an atomic weight determination with the product remaining.

I employed the classic method of weighing as silver chloride the chlorine contained in a known weight of the anhydrous chloride. As control experiment, I determined the atomic weight of barium by the same method, under the same conditions, and with the same quantity of material, first 0.5 grm. and then 0.1 grm. The figures obtained were always between 137 and 138. I thus saw that the method gives satisfactory results, even with a very small quantity of material.

The first two determinations were made with chlorides, of which one was 230 times and the other 600 times as active as uranium. These two experiments gave the same figure as the experiment with the pure barium chloride. There was therefore no hope of finding a difference except by using a much more active product. The following experiment was made with a chloride, the activity of which was about 3500 times as great as that of uranium; and this experiment enabled me, for the first time, to observe a small but distinct difference; I found, as the mean atomic weight of the metal contained in this chloride, the number 140, which showed that the atomic weight of radium must be higher than that of barium. By using more and more active products, and obtaining spectra of radium of increasing intensity, I found that the figures obtained rose in proportion, as is seen in the following table. A represents

the activity of the chloride, that of uranium being unity; M the atomic weight found:—

A.	M.	
3500	140	Spectrum of radium faint.
4700	141	
7500	145.8	Spectrum of radium strong, but that of barium predominating.
Order of magnitude, 10 ⁶ ..	173.8	The two spectra of almost equal intensity.
	225	Only a trace of barium present.

The figures of column A must only be looked upon as a rough estimate. The calculation of the activity of strongly radio-active bodies is difficult, for many reasons which will be discussed later.

At the termination of the processes described above, I obtained, in March, 1902, 0.12 grm. of radium chloride, of which Demarcay made the spectral analysis. This radium chloride, in the opinion of Demarcay, was fairly pure; its spectrum, however, showed the three principal barium lines with considerable intensity. I made four successive estimations of the chloride, the results of which are as follows:—

	Anhydrous radium chloride.	Silver chloride.	M.
I.	0.1150	0.1130	220.7
II.	0.1140	0.1119	223.0
III.	0.11135	0.1086	222.8
IV.	0.10925	0.10645	223.1

I then re-purified this chloride, and obtained a much purer substance, in the spectrum of which the two strongest barium lines were very faint. Given the sensitiveness of the spectrum reaction of barium, Demarcay estimated that the purified chloride contained only the merest traces of barium, incapable of influencing the atomic weight to an appreciable extent. I made three determinations with this perfectly pure radium chloride. The results were as follows:—

	Anhydrous radium chloride.	Silver chloride.	M.
I.	0.09192	0.08890	225.3
II.	0.08936	0.08627	225.8
III.	0.08839	0.08589	224.0

The mean of these numbers is 225. They were calculated in the same way as the preceding ones by considering radium as a bivalent element, the chloride having the formula RaCl_2 , and taking for silver and chlorine the values $\text{Ag} = 107.8$, $\text{Cl} = 35.4$.

Hence the atomic weight of radium is $\text{Ra} = 225$.

The weighings were made with a Curie aperiodic balance, perfectly regulated, accurate to the twentieth of a milligram. This direct reading balance permits of very rapid weighing, a condition which is essential in the case of the anhydrous chlorides of radium and barium, which gradually absorb moisture, in spite of the presence of desiccating substances in the balance. The bodies to be weighed were placed in a platinum crucible; this crucible had been long in use, and its weight did not vary the tenth part of a milligram during the course of one operation.

The hydrated chloride obtained by crystallisation was placed in the crucible and heated till converted into the anhydrous chloride. When the chloride has been kept for several hours at 100° its weight becomes constant, and does not change even if the temperature is raised to 200°. The anhydrous chloride thus obtained constitutes, therefore, a perfectly definite body.

The following is a series of determinations on this point; the chloride (100 m.g.) is dried in the oven at 55°, and placed in a desiccator over anhydrous phosphoric acid; it then gradually loses weight, which proves that it still contains moisture; in the course of twelve hours the loss was 3 m.g. The chloride is replaced in the stove, and the

* Thesis presented to the Faculté des Sciences de Paris.

temperature raised to 100°. During this process, the chloride lost 6.3 m.g. in weight. After being left three hours fifteen minutes in the oven, it lost 2.5 m.g. more. The temperature was maintained for forty-five minutes between 100° and 120°, which caused a loss of weight of 0.1 m.g. Then after being kept for thirty minutes at 125°, the chloride showed no diminution in weight. Then, however, after thirty minutes at 150°, it lost 0.1 m.g. Finally, after being heated for four hours at 200°, it lost 0.15 m.g. During these operations the crucible varied from 0.05 m.g.

After each determination of the atomic weight, the radium was converted into the chloride in the following manner:—To the solution containing the weighed radium nitrate and excess of silver nitrate was added pure hydrochloric acid; the silver chloride was filtered off; the solution was evaporated to dryness several times with excess of pure hydrochloric acid. In this way the nitric acid is entirely removed.

The precipitated silver chloride was always radio-active and phosphorescent. In determining the amount of silver contained in it, I satisfied myself that no ponderable amount of radium had been carried down with it out of the solution. The method I pursued was to reduce the silver chloride precipitated in the crucible by hydrogen generated from dilute hydrochloric acid and zinc; after washing, the crucible was weighed with the metallic silver contained in it.

I made another experiment which showed that the weight of radium chloride regenerated was the same as that before beginning the operation.

These verifications are not so reliable as direct experiments; but they serve to indicate the absence of any significant error.

From its chemical properties, radium is an element of the group of alkaline earths, being the member next above barium.

From its atomic weight also, radium takes its place in Mendeleeff's table after barium with the alkaline earth metals, in the row which already contains uranium and thorium.

Characteristics of the Radium Salts.

The salts of radium, chloride, nitrate, carbonate, and sulphate resemble those of barium, when freshly prepared, but they gradually become coloured.

All the radium salts are luminous in the dark.

In their chemical properties, the salts of radium are absolutely analogous to the corresponding salts of barium. However, radium chloride is less soluble than barium chloride; the solubility of the nitrates in water is approximately the same.

The salts of radium are the source of a spontaneous and continuous evolution of heat.

Fractionation of Ordinary Barium Chloride.

We have endeavoured to determine whether commercial barium chloride contains small quantities of radium chloride, which escape detection with the means of estimation at our command. For this purpose, we fractionated a great quantity of commercial barium chloride, in the hope of thus concentrating the trace of radium chloride if such were present.

Fifty kilos. of commercial barium chloride were dissolved in water; the solution was precipitated by hydrochloric acid free from sulphuric acid, which yielded 20 kilos. of the precipitated chloride. This was dissolved in water and partially precipitated by hydrochloric acid, which gave 8.5 kilos. of precipitated chloride. This chloride was fractionated by the method used for the barium chloride containing radium; and at the end of the process, 10 grms. of chloride were obtained, corresponding to the least soluble part. This chloride showed no radio-activity; it therefore contained no radium; this substance is, consequently, absent from the ores of barium.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during August has continued to be excessive. The actual amount of rain measured is 3.34 inches; the average rainfall is 2.38 inches; this gives an excess of 0.96 inch, which, added to the previous one of 8.81 inches, makes a total excess for the year of 9.77 inches, which is 62.3 per cent in excess of the thirty-five years' average. Notwithstanding this unprecedented rainfall the soluble organic matter in the Thames-derived supply, which has been exceptional in amount during the last few months, has now sunk considerably. The organic carbon per gallon, which in June was 0.189 and in July was 0.155, was reduced in August to 0.148 grain—only a trifle in excess of the average amount over the whole of last year, an exceptionally dry one.

Our bacteriological examinations of 370 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 360 others from special wells, standpipes, &c., making a total of 730 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	270
New River, filtered (mean of 71 samples) ..	15
Thames, unfiltered (mean of 25 samples) ..	10,910
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples) ..	43
Ditto ditto	highest 372
Ditto ditto	lowest 0
River Lea, unfiltered (mean of 24 samples) ..	189
River Lea, from the East London Water Com- pany's clear-water wells (mean of 25 samples) ..	33

Of the 296 daily samples taken from the filter wells of the Metropolitan Water Companies, five samples, or 1.6 per cent, were sterile. There were thirty-eight samples, or 12.8 per cent, containing more than 100 microbes, and of these, nineteen samples contained more than 150 microbes per c.c. The thirty-eight excess samples contained an average of 180 microbes per c.c.; in July ten excess samples contained an average of 159 microbes per c.c.

When we take into consideration the entirely abnormal weather experienced during the present summer, the con-

ditions of the supply from the bacteriological point of view must be pronounced, on the whole, satisfactory.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS

Synthesen in der Purin- und Zuckergruppe. ("Synthesen in the Purin and Sugar Groups"). By EMIL FISCHER. Braunschweig: Friedrich Vieweg und Sohn. 1903.

THE application of synthetic methods to the solution of biological problems is continually becoming more extended, and apparently fruitful of results, and the questions briefly touched upon in this lecture, which was delivered before the Swedish Academy of Science in Stockholm in December, 1902, cannot fail to excite the interest of all into whose hands it falls. The difficulties of explaining the outlines of such a subject as the above to a mixed audience, not composed of specialists, might fairly be regarded as almost insurmountable, but this able popular exposition shows what an enthusiastic lecturer can do, and the admirable blending together of history, experimental truth, and inspired forecast forms the type of lecture most likely to appeal to the critical faculties and imaginations of the hearers. Butlerow's and Kiliani's famous researches on the sugars are briefly described, with special reference to their applications to such questions as the action of the enzymes and the assimilation of the carbon dioxide of the atmosphere by plants, and nothing could show more plainly the powers of the great master of organic chemistry than the excellence of this lecture on a difficult, and, from some points of view, an abstruse subject.

Cyanid-Prozesse zur Goldgewinnung. ("Cyanide Processes for obtaining Gold"). By MANUEL VON USLAR and Dr. GEORG ERDWEIN. Halle-a-S.: Wilhelm Knapp. 1903.

THIS book deals with the various modifications of the cyanide process, which may truly be said to have influenced methods of gold extraction to an extent only comparable in the metallurgical world to that of the Bessemer and Thomas-Martin processes in the iron and steel industries. Considerable space is devoted to the consideration of the chemistry of the changes involved in the process, which is well explained, and the most minute details of the many modifications of the original method are recorded. The information relating to the cost and output of the process has been drawn in all cases from reliable sources, and includes the description of the plant of some of the most important mines in the Transvaal. This volume appears to be quite up to the level of the preceding in the series of Monographs on Applied Electrochemistry, and experts will find it a very complete and useful guide.

Mechanism of the Substitution of Bromine.—Ludovik Bruner.—It is known that the presence of a little iodine facilitates the substitution of bromine for hydrogen in aromatic compounds; the author, examining the mechanism of this reaction, explains it by means of the dissociation of the bromide of iodine, and the bromising action of the atoms of free bromine which result from it. He examined more particularly the bromisation of benzene in the presence of iodine, and proved that its progress was that of a quadrimolecular reaction, $C_6H_6 + 4Br = C_6H_5Br + HBr_3$. He examined also the catalytic action of some other "bromine fixers" on the coefficient of speed. In some cases he measured the relative speeds of instantaneous reactions, and showed, in so far as it concerns the bromisation of phenol, of bromophenols, and of aniline, the parallelism existing between the speed of the reaction and the electrolytic dissociation. —*Zeit. Physik. Ch.*, vol. xli., p. 413.

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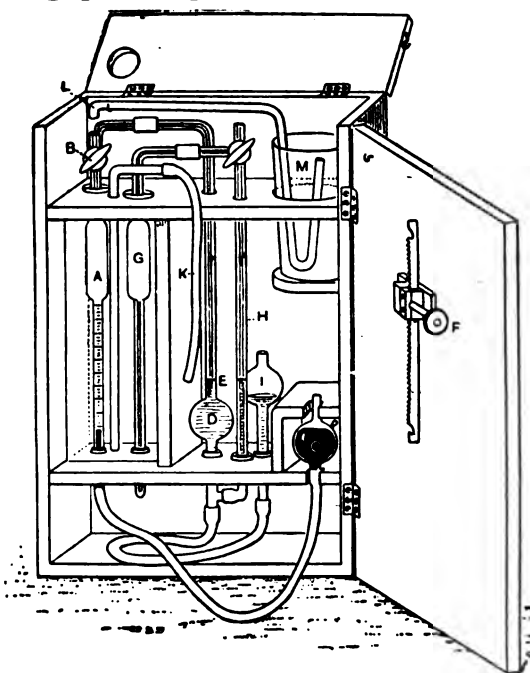
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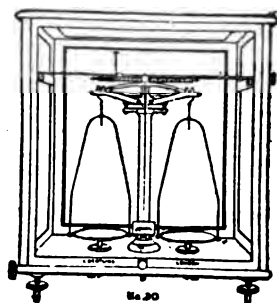
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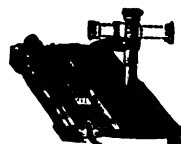
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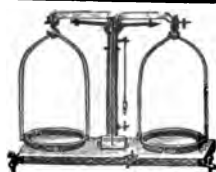
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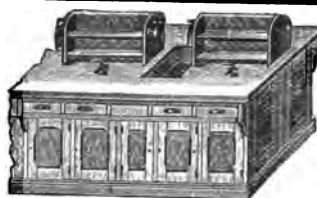
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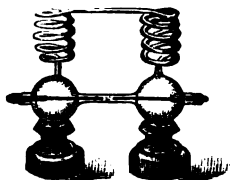
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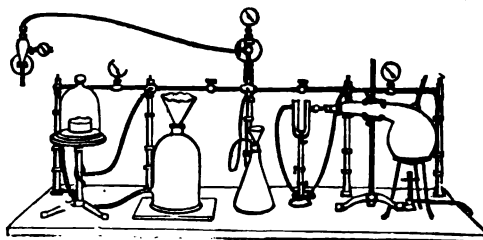
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THE CHEMICAL NEWS.

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ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

SOUTHPORT, 1903.

By CHARLES VERNON BOYS, F.R.S.,
President of the Section.

(Concluded from p. 159).

It is impossible not to be struck by the similarity both of phenomenon described and of language used in this paragraph and in almost any of the papers on radium. I know this mere superficial similarity is worth very little, if anything; but for centuries the sky has shown us a phenomenon still not entirely understood, and the inability to remove all difficulty by the aid of radium or similar material is no reason for dismissing the idea of connexion without further thought.

The comet's tail is still a mystery. Let me take the most recent explanation, which was set forth only three months ago in the *Astrophysical Journal* in the United States. Those admirable experimentalists Nichols and Hull have for some years been investigating the back pressure exerted by the action of light upon bodies on which it falls. In this they have followed the Russian physicist Lebedew, but in minuteness and delicacy of measurement, and in their successful elimination of disturbances, their results are unequalled. It is sufficient to say that, difficult and minute as the experiment is, their success is such that the discrepancy between the calculated force and that which they have found is under 1 per cent. Perhaps I may express some satisfaction that in this measurement use was made of the quartz fibre.

Having now definite and accurate confirmation of the existence of the force produced by the action of light, or rather radiation, Nichols and Hull proceed to examine the question as to how far such repulsion may be competent to overcome the gravitative attraction of the sun and drive away the matter which pours out from the comet. It is interesting to note here that Kepler put forward this very idea, and that Newton, the inventor of the corpuscular theory of light, looked upon the suggestion with some favour.

Coming now to this recent paper of Nichols and Hull, we find first the consideration of the relation of the attraction by gravitation, and the repulsion by light upon particles of different sizes and densities. Density has no influence on the action of light, while it is favourable to gravitation, and therefore unfavourable to tail formation. Size is favourable to both, but more to gravitation than to light, for if the diameter of a particle be doubled, one is increased eightfold and the other only four. So size favours gravitative attraction. Conversely, of course, smallness favours repulsion by light, which relatively should get greater and greater as the particles diminish in size. At last, then, a degree of smallness may be reached in which the repulsion by light will actually be equal to the attraction by gravitation, and such a particle would remain in space, its motion unaffected by our sun. Let the diminution of size continue, and then the repulsion will be in excess, and if the law were to continue it would with sufficient diminution become relatively as large as we please.

The law, however, does not continue. Schwarzschild has shown that when the particles are small enough, light does not act upon them in the same way. Owing to diffraction, the effect of light is unduly great for a certain

very small size of particle, while it fails almost entirely when the particle is made much smaller. Thus it is that the indefinite increase in the repulsion by light as compared with the attraction by gravitation with diminution of size of particle is checked, and when, according to theory, with a particular density of particle, the light pressure is about twenty times as great as gravitational attraction, further diminution of size ceases to favour the action of light, and it begins to fall off again. The distance of the particle from the sun has no influence upon the relation between the two kinds of forces, for they rise and fall together. Nichols and Hull, therefore, while not denying that other causes may operate, believe that light pressure is adequate to account for the phenomena, and that where the material coming from the head or comet proper is of two or three kinds, whether of density or of size of particle, the separation of the two or three tails should naturally follow.

This theory presupposes that the nucleus of a comet will be able, owing to the evolution of gas under the sun's heat, to send out enormous quantities of dust, the finer and lighter the better, so long as it is not unduly small with respect to a wave-length of light. Such dust would account for any reflected solar light that the spectroscope may show, but it is not easy to see how the spectrum of hydrocarbons, of sodium, and of other metal, should be produced for lack of temperature. It is not easy to see why fortuitous dust should be graded of such sizes as to give well separated and defined tails; it is not easy to see how the dust could be produced in sufficient quantity to provide visible illumination to millions of millions of cubic miles of space through which it may be passing at ultra-planetary velocity, even though in looking through a million miles or so one grain of dust in a hundred miles might suffice to supply the light.

Other theories of the comet's tail require an electrified sun, the existence of which is explained by Arrhenius as being caused by the emission by the sun of negatively charged electrons which, picking up condensing gases as Aitkins's dust picks up moisture from the atmosphere, are driven away by the light pressure. Arrhenius believes that these acting on the matter in the tail would give rise to the bright line spectra which have been observed. The result of all this escape of negative electricity is a positively charged sun, but what limits the charge in the sun it is difficult to see, as it is, why the electrostatic attraction helped by gravitation does not ultimately stop the action. I may be displaying my ignorance, of which I am sufficiently sensible, but I am not aware of any evidence for the existence of the stream of electrified grains or drops imagined by Arrhenius.

Nichols and Hull, while calling to their aid the researches of Schwarzschild to give them a repulsive force some twenty times as great as gravitative attraction, do not seem to have given due weight to the extremely small range of size of particle for which this high effect is available. The maximum effect for any wave-length, according to Schwarzschild, is produced when the size is such that a wave-length will just reach round it; that is, with ordinary light when the diameter is between one hundred thousandth and one hundred and fifty thousandth of an inch. If the diameter is two-and-a-half times the wave-length, the action of light is only equal to gravity with a material of the density of water; or, again, if it is reduced to one-eighth of a wave-length it again becomes equal, and in these two cases there is no resultant action. With either larger or smaller particles gravity rapidly gets the better of light, while the high advantage of light over gravity is confined to very narrow limits.

What the sifting process can be that will give rise to such a quantity of this microscopic dust we can hardly expect to be told, nor why even if the material should in some mysterious way be graded, the ungraded wave-lengths of the solar spectrum should allow of the marked separation in some instances of comets' tails.

One thing, however, they do assert, and that is that the

light pressure can have no action on a gas, so that if what we see is considered to be gaseous the light pressure theory must be thrown over for some other.

I cannot leave this excursion of Nichols and Hull into a speculative domain of science without expressing my admiration of the experimental work which they have accomplished, or of my appreciation of the ingenuity and daring with which they have attempted the hitherto unheard of feat of making a comet.

While the theory just referred to may be the most recent, it must not on that account be supposed to displace all that has gone before; the authors themselves do not suggest this; it is the last thing that would occur to them. They have referred to the researches of Bredechin that occupy so large a proportion of the annals of the Observatory of Moscow.

It is impossible to read even a tithe of these without feeling that the subject of comets and their tails is one which Bredechin, by his amazing industry, has made his own property, and that any stranger casually passing by and taking a random shot should receive the severe penalty awarded to poachers in this country. Bredechin has dealt unmercifully—I do not say unjustly—with the author of at least one such random theory.

It is therefore with the greater diffidence and more urgent plea for forbearance that I venture to draw certain parallels and hazard certain suggestions which I admit freely have not reached a stage at which detailed comparisons with known comets are possible.

It does not seem possible now to contemplate the phenomena of the comet, of the divided tails, of their tenuity and transparency, of the pale luminosity, partly reflected solar light, partly light as from a glowing gas; of the gradual wearing out and disappearance of those comets which constantly pay visits to solar regions, with all the mysteries of radium now so much in evidence without tracing the features in which they resemble one another. By radium, of course, I mean any material with the remarkable radio-active properties that radium exhibits with such pre-eminent splendour, whether known in the laboratory or not.

How many physicists have been peering at comets through radium spectacles, or how many astronomers detect the sparkle of radium in the fairy tresses of their hirsute stars I know not. One writer, however, T. C. Chamberlin, so long ago as July, 1901, looked upon a connexion between radio-active materials such as were then known and comets as at least worth considering. Chamberlin's paper in the *Astrophysical Journal* was mainly on the tidal disruption of gravitating bodies and the possible evolution of comets, nebulae, and meteorites, and he did not pursue this consideration in any detail; indeed, the enormous accumulation of new properties of radium was not then available.

Whatever may be imagined as to the constitution of a comet, difficulties still remain. All I suggest now is that the curious properties of radium and of similar bodies should be kept in mind. Radium at least supplies the means by which, if the increasing warmth or the tidal action of the sun should awaken its activity, Rutherford's α -rays should be shot out at the speed that he has measured of a thousand million inches a second, i.e., one-twelfth the velocity of light. These α -rays, according to Rutherford, consist of helium; they weigh each twice as much as a hydrogen atom, and so the same weight of comet matter that would make one of Nichols and Hull's best particles, i.e., one that would be just visible with a microscope, would be sufficient for about 400 millions of Rutherford's α -ray particles, an advantage surely where diffuseness seems so miraculous.

These particles, shot out at a velocity one-twelfth that of light, go so fast that, if they were to start horizontally on the surface of the earth, the gravitative attraction of the earth would curve their path to the infinitesimal extent of a curve with a radius of forty-thousand million miles. Yet so great is the electric charge they carry that a visible

curvature can be imposed upon them in a practicable electrostatic field.

Now imagine these transferred into space at a distance from the sun, for instance, equal to that of Venus. Gravity there due to the sun is only one-thousandth of what it is here, so gravity there would be, to the same extent, less able to impose visible curvature on their paths. But their electric charges are still available, and unless I have made an arithmetical blunder of a considerable order, it would require no very heavy electrification of the sun to bend these rays round in a curve with a radius of 1000 miles. An electrostatic field of under two ten-thousandths of a unit should be sufficient, a field which would be produced if the sun were only charged with a surface density of one electrostatic unit on every three square centimetres.

Whether these figures are correct or not—and I know the risk of getting just thirty-thousand-million times too large or too small a result—does not much matter. An electrified sun, which after all others besides Arrhenius have postulated, would be sufficient to turn the rays and send them away at rapidly increasing speed so as to form the tail. The speed would in a short time reach the velocity of light if it were not for the change in properties of matter which supervenes when any such velocity is nearly reached. Thus, according to the ratio of charge to mass, particles such as Rutherford's α -rays would be sent away each with its limiting velocity, giving rise to streaks more or less well-defined, and double, triple, or multiple according to the number of kinds of ray which the various radio-active materials were able to generate.

Not only should streaks pointing away from the sun be formed, but any negatively charged rays, such as radium is said to give out, should form a tail directed towards the sun. Perhaps this might be expected to be general, but while not common one was described by Hind in the comet of 1823-24, and three or four more have been observed.

The head or coma would be the envelope of all the independent orbits, leaving the nucleus in all directions—orbits which, while their velocities are still of the Rutherford order, would be hyperbolas convex to the sun.

If this should not appear to be absolute nonsense it would seem as if another difficulty should become less than it has been. I refer to the visibility, luminosity, and spectral character.

Lodge, as an interpreter of Larmor, tells us that an electrified ion subject to acceleration, whether transverse or in the line of motion, radiates energy. The streamers from the nucleus subject to the greatest acceleration may be bright almost as the nucleus itself; then, as they have become dissipated into regions where far less acceleration becomes possible, the radiation falls off and the tail is lost in space.

The observations made last month by Sir William and Lady Huggins of the spectrum given by a piece of radium in the air may have some bearing upon the luminosity of the comet. It is possible that the internal motions set up by the separate parts, each pursuing its individual orbit, may produce collisions numerous and violent enough to account for all the light that is seen, and for temperature sufficient to bring out the spectral lines that have been identified. Whether this is so or not, radio-active bodies and their emanations can produce light independently of such action; and now these observers have found that in the case of radium in air this light gives the spectrum, line by line, of nitrogen. It is possible that the enveloping nitrogen has had its atoms so harried by the activity of the radium as to give a response hitherto only awakened by electric discharge? The ability to obtain such a response opens up a new possible interpretation of these spectra, which hitherto have been assumed, with our laboratory experience only to guide us, to have required for their production temperature above a red heat. If further observations should confirm this, the hydrogen, the hydrocarbon, and possibly even the sodium or iron spectrum that has been observed, may have come from cold atoms; and it is not even quite beyond the limits

of imagination to picture, not from the comet matter itself, but from loose residual and highly attenuated matter through which the comet is passing.

There is one other feature of this remarkable observation of equal interest. The lines of the spectrum were not exactly in their proper place, but were all shifted towards the red end of the spectrum about twice the distance between the D lines. If only one or two lines had been so observed a different origin might well have been suspected; but when the whole series are faithfully reproduced it is reasonable to look upon the spectrum as modified to that extent as though the works of the nitrogen atom had not only been set in movement, but had been loaded with the radium emanation.

Before dismissing these random speculations on the possible connexion between radio-activity and comets I would ask your leave to refer once more to Bredechin's conclusions. He has found that it is merely necessary to postulate three kinds of matter, issuing from the nucleus with three initial velocities, and subject to repulsion from the sun with three sets of forces of repulsion—i.e., as compared with ordinary gravitative attraction—for the whole of the phenomena of all sorts of comets to be very completely accounted for. His highest initial velocity is only about five miles a second, and his lowest about a quarter of a mile a second. His highest repulsion, after deducting gravitative attraction, is only eleven times gravity, and his lowest only a fifth of gravity. If, then, with such velocities and forces the phenomena can be exactly accounted for, it would seem futile to consider the possibility of initial velocities from 4000 to 80,000 times as great and effective repulsions of a corresponding order being able to produce effects with anything in common. This is not necessarily the case, for with the comparatively slow separation of the atoms of Bredechin's matter from the nucleus, each one describing its own hyperbola convex to the sun, the tail at any moment represents the then position of any number of atoms which left the nucleus for some distance back, whereas with the enormous velocities and effective forces now discussed the comet moves so slowly in comparison that the tail would practically represent the path at the time.

It has taken me far longer to throw out this not very luminous ray than I had expected or than it is worth. I fear that it is a sort of ray in which the ratio of its dead weight to its vitalising charge is too small to enable it to penetrate the lightest screen of examination.

These are the days of rays, and now before we have quite become familiar with the rays of radio-active bodies Blondlot has presented us with N rays which issuing from the mantle of an incandescent gas-burner penetrate wood or aluminium, and then increase the light without increasing the heat of hot bodies on which they fall.

Passing now from the amusement of speculation to more serious duties, I find myself confronted with the difficulties that prevent us in this country from succeeding as we used to do in the international struggle—a struggle the issue of which is daily becoming more and more a question of brains, of education, of skill and enterprise in manufacture—and finally of that great virtue extolled by the President of the United States, strenuousness.

It is the duty of everyone who sees the way in which we are being outstripped in the race to do what in him lies to scrape off the rust which is clogging our educational machinery. I now refer to the defects which hamper the intellectual progress of the majority of our youth. I believe the public school mathematics in this country stands on a level of its own, well below that of any other. In England, owing to our complicated system of weights and measures, which our Ministers and our Parliament dare not abolish for our own good, the scanty hours allowed for mathematics are devoted to the learning of tables which should never have to be learned at all, to compound reductions designed merely to puzzle but not to lead to any new step; and,

even if our present system were not futile enough, to learning lists of antique values which serve the useful purpose of giving the boys something to do. The result is that beyond having time to acquire a few elementary algebraical rules the boy is never introduced to algebra proper; he has no idea of algebraical reasoning; his trigonometry often does not exist, and the very sound or suggestion of co-ordinate geometry or of the differential calculus, which might be well within his reach, produces a shiver of dismay. Geometry is presented for the first time in the form of Euclid, a form as repulsive to most boys as it well could be. I must confess to having been attracted and not repelled by Euclid; but the boy does not care for time. Now that I look at Euclid again I have also to confess that any lingering regard for an old friend vanishes before the archaic language and the unnecessary circumlocution. If Euclid must be retained let it be translated into English, the English that any parent would use in explaining the ideas to his son; let it be illustrated by constant reference to real things so as to appeal to the boy who does not revel in the abstract. Let the ideas and the terms first be presented in the form of experiments and of measurements with instruments; let the schoolmaster dare to throw over the intolerable conservatism which prevents our doing anything ten times as well lest some item should prove to be a trifle worse; in fact, let us take some heed of the possibly extreme, but none the less genuine, and valuable preaching of Professor Perry. I have so far referred only to the miserable use that is made of the odd hours grudgingly given to what is called mathematics. Is it any use to repeat the long-standing complaint of the way in which the schoolmaster insists upon overdoing his Latin and Greek under the belief that they are at least essential to intellectual development if, indeed, they do not supply the only stimulus? As society is constituted they are essential to education as an extensive knowledge of Confucius is essential to an educated Chinaman, so that we may mix one with another, appreciate the works of our great authors, understand the same allusions, and have the same kind of knowledge of the development of our civilisation. Few men of science, perhaps none, wish to see all of this, some of which is essential to a general education, abolished; all that we ask is that the schoolmaster shall not continue to impose upon the community the unbalanced learning which corresponds to mathematics and science without letters. The time given to classics is exorbitant; more must be reserved for those pursuits which draw out the habit of independent thought, creation, and originality. It would be well if every schoolmaster could read an admirable article by James Swinburne on the two types of mind fostered by the two complementary types of education, but this is buried away in an inaccessible number of the *Westminster Review*.

The classic is unfortunately still in possession, and where, as is still often the case, he is innocent of any appreciation of the educational value of post-Newtonian studies it is not surprising that he thrusts into odd moments the subjects he does not understand, and which he therefore despises, and that the boys committed to his charge and living in such an atmosphere are half ashamed of showing any interest in the scanty science which is within their reach. It is almost impossible to believe that such can be the case, but I have referred to the impression to which the appointment of the first science master at my own school gave rise. I now refer to the contribution to a discussion on education but a year or two ago by that experienced teacher, Principal Griffiths. Fortunately our public schools are not the only ones in the country. Smaller and less fashionable schools pay more attention to education and suffer less from what, in defiance of all rule, I can only call didactical method.

I am not aware that the result of this almost total exclusion of tabooed subjects in favour of Latin and Greek is producing a standard of classical attainment in our youth greatly in advance of that to be found in other countries, but it is certain that in history, modern languages, mathe-

matics, and science the product of our public schools is sadly deficient.

There is another point related to our deficient general scientific training on which I wish to offer some remarks, and that is in relation to manufacture. It is the fashion among some of our scientific people to talk of our manufacturers as if they were a very ignorant lot and to suppose that one word from some professor who has never seen outside a laboratory would be sufficient to put them right. Now in my somewhat varied experience I have had occasion to become acquainted with corners of our great manufacturing areas, and while my experience is small and not enough to generalise upon, it is nevertheless several times as great as that of some who are ready to adopt the superior attitude, but have none.

The loss of one industry after another is only too patent. In so far as this may be due to want of enterprise in our men of business we are not concerned with the cause in this Section; in so far as it may be due to want of that little assistance which the fiscal arrangements in other countries make possible for our rivals, again we are not concerned in this Section; in so far as our patent laws are unique among those of manufacturing nations in allowing the foreigner to manufacture in his own country under the protection of our patent law, so that the most valuable school we possess, the manufactory, as well as the manufacture, is conducted to the advantage of our rivals—a point which I suppose it is unnecessary to commend to the notice of Mr. Chamberlain—with this, too, we have no concern in this Section; but in so far as this, or the want of enterprise or of foresight that leads to it, is due to ignorance and to want of appreciation of scientific advance, we are very much concerned with it. If I may refer to my own limited experience, there is a lamentable contrast in the manner in which a great number of our own countrymen look at any proposition put before them and that in which the alert American does. It is useless to explain that which would be self-evident to a man with a moderate knowledge of chemistry and physics such as our schools ought to supply, or for which they should at least lay the foundation, for the words have no meaning; they are merely words. He distrusts anything new; he has heard of a new process before that did not work out well; experience on the Continent to him is no experience at all, for he believes the inhabitants in such distant parts of the earth are not capable of knowing as well as the enlightened Englishman whether a thing is properly done or not, and so he goes on as he did before, perfectly content. This attitude would not be possible with the most elementary understanding of common principles.

But there is another side to this picture. Anyone who has discussed any scheme with the board of directors, the manager, the engineer, and the chemist of one of our great manufactories must have been struck with the concentrated ability there found in harness. It has often seemed to me that it is a great misfortune that our professors of mechanics, of physics, and of chemistry are in so many instances precluded from a better acquaintance with the working of these great machines—a misfortune not for the works, at least directly, but for the professors, and more especially for their pupils.

Nowhere are scientific problems of greater complexity constantly having to be solved than in a great manufactory; nowhere is such concentrated talent necessary as in a works organised and carried on in competition with all the world. I look upon these as our most valuable schools, and the closer the touch between them and those whose province it is to teach, the better for the teacher and the pupil.

It is, perhaps, hardly desirable to mention any one where there are so many. I am tempted to dwell upon the problem which has been at last successfully solved by Parsons, this being the joint product of the school and of the works; but there is one picture—a contrast, I will not say of light and shade, but of colour and colour—to which I must refer. I remember in my early days, in the sur-

roundings of a classical atmosphere, the general feeling of contempt for the manufacturer, the intellectually inferior creature who only made money, but who knew nothing of *τέχνη* or *εὐφυΐα*. I am not sure that some such feeling does not still exist among those whose horizon is limited to the Latin and Greek that they have learned—or should I say limited by instead of to? This recollection came back to me when not long ago I was visiting one of the best organised and most skilfully conducted works in the country—I mean Willans and Robinson—when I remembered that another great manufactory, conducted on American lines, was near by, and when across the road I saw the walls of one of our most famous English schools. I pictured the old contrast: on the one hand, the conviction impressed upon me when a boy that there is something intellectually superior in the struggle with a paragraph of *Xenophon* or a page of *Homer*, while manufacture is merely mechanical, sordid, and base, with what I believe to be the reality on the other. I wondered in what spirit the erection of these works was viewed at the school, and to what extent the high intellectual attainment there so essential and so evident is properly appreciated.

Of the last of the three headings, *Strenuousness*, we have plenty, but at school it is most apparent in cricket and football, and in after-life in various expensive ways of murdering defenceless animals.

However, a change is already beginning to be felt. The public schools no longer withhold the elements of chemistry and physics, and those who have benefited, even in small degree, are taking responsible places vacated by those who had no such opportunity. The numerous polytechnics are providing more serious instruction to thousands of our young men, and it may be hoped that in time even the official—I mean the mere official whose only conception of activity is centred in obstructing progress and enlightenment—will have some appreciation of things as well as of words.

COSMICAL RADIO-ACTIVITY.*

By ARTHUR SCHUSTER, F.R.S.

THE fact that every physical property hitherto discovered in one element has always been found to be shared by all suggests the possibility that radio-activity may be a common property of all matter. If that is the case, the so-called radio-active bodies may only be distinguished from others—like iron in the case of magnetism—by the enormously exaggerated form in which they possess the property. The apparently inactive metals may possess radio-activity, but to so small a degree that our powers of observation are insufficient to detect it. But the question arises whether in that case the effect is cumulative and should appear in the large cosmic aggregations of matter.

There is indeed at first sight some analogy both in the case of the sun and of the earth between the effects observed in their immediate surroundings and those noticed in the neighbourhood of radio-active bodies. The earth we know must be charged with negative electricity, and attention had already for some time been drawn to the fact that this charge must constantly be renewed, as the leakage due to the spraying of ocean waves and the hot gases escaping from every chimney would ultimately dissipate the charge. But the normal electric conductivity of the air has only recently been measured, and, according to Elster and Geitel, is, under normal conditions, such that a body loses about $1\frac{1}{2}$ per cent of its charge per minute. If the air in the immediate neighbourhood of the ground has this conductivity (which is not quite certain) the earth would lose about half its charge in an hour.

We are living therefore—and there can be little doubt about the point—in an electric field through which nega-

* A Paper read before the British Association (Section A), Southport Meeting, 1903.

tively charged particles are constantly driven outwards (cathode rays), and which possess an electric conductivity similar to that found in the neighbourhood of radio-active bodies. The radio-activity of air rising out of the ground or of water drawn out of wells may be the consequence of emanations from a radio-active earth.

The similarity of the rays of the solar corona to cathode rays has often been pointed out, and I have maintained for a long time now that the assumption of a greater conductivity of space at times of maximum sun-spots furnishes a simple explanation of the connection between sun-spots and terrestrial magnetism. The sun therefore, like the earth, must be taken to discharge rays which seem to possess all properties of cathode rays.*

The analogies I have pointed out are not complete, and may be found to be false; but we must, I think, keep our mind open to the possibility of a collective radio-activity of matter which becomes apparent in celestial bodies.

The continuous discharge of negative electricity from the earth renders it necessary to find a cause leading to a continuous renewal, and it is extremely difficult to see what that cause can be.

Though not directly connected with the subject under discussion, I may, in conclusion, digress by recalling an old discussion on the cause of gravity. Lesage's explanation involved the presence of "corpuscles," such as are now believed to exist by some physicists. Maxwell's objection to Lesage's explanation, which at the time seemed fatal, was that gravitation ought to be, but is not, accompanied by a rise in temperature. Whatever we may think of the explanation on other grounds, this particular objection would seem to lose its weight at present, when, in the case of one body at any rate, a rise in temperature above that of its surroundings has actually been discovered, and when it is considered that the energy which in one case accumulates as heat may in other cases be dissipated through other channels.

GRANULAR AND SPICULAR STRUCTURE IN SOLIDS.†

By G. T. BEILBY.

In a communication made to the British Association in 1901 ("Report," 1901, p. 604) I drew attention to certain facts which had apparently escaped the notice of other observers in micro-metallurgy.

It was shown that transparenence in metals is not only found in such specially attenuated forms as thin leaves or films deposited on glass, but that it is an intrinsic property of the metal even in its more massive forms. It was further shown that metal surfaces under obliquely-reflected light exhibit a remarkably uniform granular or spicular structure, which appears to be quite distinct from the crystalline structure revealed by the etching methods of micro-metallurgy.

During the past two years my study of this subject has been continued and extended, and some of the results have been already published (*Royal Society Proc.*, vol. lxxii., No. 481).

The object of the present communication is to place on record such confirmation and modification of the original observations and statements as have resulted from the further study of the subject.

The original statements depended on microscopic observations made by obliquely-reflected light with objectives of moderate numerical aperture. This form of illumination

can only be conveniently applied with objectives whose working distance is not less than 5 m.m., and whose front lens is not very large. It was therefore desirable that the observations by obliquely-reflected light should be supplemented by others, in which different methods of illumination could be employed.

A study was made of films of metal which were thin enough to transmit light freely. By transmitted light, if such films are not too thin, they show a distinct granular texture, as if the substance had been partly gathered up into minute mounds. By alternatively illuminating one of these films by transmitted and by obliquely-reflected light, it is seen that the structure which is granular by the one light is spicular by the other; the spicular appearance, therefore, is caused by a granular texture. The slightness of this texture is shown by the fact that it is visible by oblique light in metal films which are less than 10 μ in thickness.

By a parallel study of the surface layer in metals in their more massive forms, it was found that this layer is, in many respects, distinct from the mass which it covers, being in its structure and properties similar to the thin films deposited on glass.

The character of the material on which the film is supported has a considerable influence on the appearance by obliquely-reflected light. In the case of massive metal, the opaque highly-reflecting under-surface adds a light and colour to the spicular appearance, which is absent in that of the thin glass-supported films. But, if due allowance is made for this, the correspondence between the appearance of the two, the surface layer and the thin film, is so exact as to leave no doubt as to the identity of the structure which causes this appearance.

The transparenence of thin films of metal was studied by Faraday, and some of his conclusions have been confirmed by subsequent observers. His very remarkable observations on the effect of heat annealing on thin films appear to have dropped out of sight. The subject has been studied by me with the help of lenses of a resolving power much greater than any which could be obtained in Faraday's time. The results of these recent observations confirm and extend Faraday's conclusions, and it is believed that they also supply an answer to certain questions which he raised.

The condition of greatest opacity is found in metal films which are in a state of strain, and the condition of greatest transparenence is found in films which have been relieved from strain by annealing. Contrary, therefore, to the generally accepted idea, the metal in gold leaf is in its most opaque condition.

Increase of transparenence in metals is accompanied by diminution of reflecting power and *vice versa*. This effect can be seen most distinctly in translucent films, but it is also quite evident in the surface of the more massive forms of metal. Films of gold and of platinum 200 μ in thickness have been obtained which are translucent and optically continuous. Films less than 10 μ in thickness have also been made which appear to be equally continuous, and are perfectly transparent. The thinner films are practically without metallic reflecting power, while even in the thicker films the reflection is distinctly inferior to that of gold leaf.

The process of annealing has been watched on the surface of metal, and the phenomena were found to be similar in kind to those which occur in films supported on glass or mica. In surface films also the increase of transparenence was well marked, and the return of the metal to the more lustrous, but less transparent, condition by burnishing was evident.

From the study of the phenomena observed in cutting, polishing, burnishing, and annealing, I have been led to the conclusion that the disturbance caused by these operations temporarily confers a degree of freedom upon the molecules of the surface layer, which enables them to act like a viscous fluid, subject to the influence of the molecular forces as they manifest themselves in surface tension. The dimensions and the forms of the grooves, ridges, and granules on the surface give a general indication that the

* The slight diminution of temperature at times of maximum sun-spots, which seems to be indicated by recent discussion of thermometer readings, may be a result of the increased absorption in space which we must expect to be caused by the presence of a sufficient number of electrons.

† Abstract of a Paper read before the British Association (Section A), Southport Meeting, 1903.

layer affected by this freedom and by the surface tension is many molecules in depth.

It appears probable that the granular structure of the surface is largely a result of surface tension. A similar structure can readily be developed in a very thin film of a viscous fluid. If a little oil is spread on a slip of glass and then almost completely wiped off, so that it is barely visible to the unaided eye, a granular film is produced which gives a well-marked spicular appearance by obliquely-reflected light. A film of varnish on a non-reflecting support shows the same structure. A thin film of fuchsin on glass shows a structure and a play of colour which might almost be mistaken for that of a feebly-reflecting gold film. Films of oxide or sulphide on metal surfaces show the spicular appearance very brilliantly.

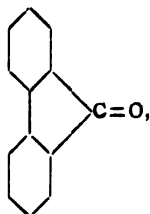
This surface granulation appears to be almost universal, and I have never failed to produce it in any solid with which I have experimented.

Granular or spicular structure seems to be closely associated with the deposition of solids from solution. It is seen in thin films of metal deposited either chemically or electrolytically. In precipitates formed in very dilute solutions there are three stages in the appearance of the solid:—(1) Spicules or spicular films of extreme thinness, (2) granules, and (3) crystals. Spicules may be formed singly, but they often result from the breaking up of the thin films which are formed at the surface of contact of the two reagents. Their pedetic movements lead to their agglomeration into granules, which sink to the bottom of the containing vessel, where they become centres of attraction to the moving spicules and grow by their absorption. Till the granule has reached a certain size and mass it shows no indication of crystalline form or structure, and its form remains, under the control of surface tension, rounded and granular. When a certain size is reached, the crystallic force begins to assert itself and to overpower surface tension, and the rounded form begins to develop faces and angles till, finally, a well-developed crystal is produced.

ON SOME DERIVATIVES OF FLUORENE.*

By Miss IDA SMEDLEY.

ASSUMING, as Professor Armstrong has contended, that all visibly coloured substances contain three separate light-absorbing centres which co-operate in producing the colour effect, the determination of the nature of the radicles which can act as such centres is of importance (compare "Encyc. Brit.," xxvi., 745). A series of fluorene derivatives has therefore been studied with the object of ascertaining the change in colour produced by the introduction of different radicles. Fluorenone,—



being a coloured ketone, was chosen as the starting-point from which to prepare compounds containing the radicles $>CCl_2$, $>CS$, in place of the carbonyl group.

The chloride prepared by the action of phosphorus pentachloride on fluorenone is a colourless compound. In the derivatives of hydrindonaphthene and of naphthalene prepared by Zincke (*Ber.*, xx., 2053; xxi., 3540), the displacement of the carbonyl group by the group $>CCl_2$ is also attended by a loss of colour. It would appear, there-

fore, that the radicle $>CCl_2$ does not function as a "colour-centre."

Thiofluorenone was prepared by the action of K_2S on fluorenone chloride. The substitution of the thio-carbonyl for the carbonyl group is accompanied by an increase in colour, an intense red compound being formed instead of the orange-yellow fluorenone. The colour of the thio-ketones is of special interest, since thiobenzophenone and the substituted thio-benzophenones are deep blue, and all give violet solutions (*Ber.*, xxviii., 2869). The co-operation of the thio-carbonyl group with other centres is necessary, since, in compounds such as thiourea, the presence of this group alone is insufficient to condition colour. The greater tendency of the radicle $>CS$ to produce colour, when compared with the carbonyl group, is probably connected with its more unsaturated character as shown by the ease with which disulphides are formed. The disulphide of fluorene has been prepared, and like other known disulphides is colourless.

ACTION OF DIASTASE ON THE STARCH GRANULES OF RAW AND MALTED BARLEY.*

By ARTHUR R. LING.

THE whole of the published data referring to the hydrolysis of starch by diastase have been derived from the study of the action of the enzyme on potato-starch paste, and the application of these to practical purposes has led to misleading and erroneous conclusions. The starches of barley and other cereals differ from that of the potato in being readily attacked by a solution of diastase in the ungelatinised condition.

The author has carried out a series of mashes with barley and malt starch of various origin, the starch being mixed with the diastase preparation in the dry state and mashed with water at different temperatures for two hours.

The following table illustrates the results obtained:—

Starch employed.	Mashing temperature.	$[\alpha]_{D^{20}}$	*R ₈₈
Barley, 1899 sample	60°	140.8	88.7
" " "	65.5	143.4	88.2
" " "	71	145.1	80.6
" 1902 sample	60	150.7	84.2
" " "	65.5	152.3	79.0
" " "	71	163.8	77.8
Kilned malt	60	150.9	84.4
" " "	65.5	156.1	80.6
" " "	71	161.3	67.2
Low-dried malt	60	151.6	85.3
" " "	65.5	152.5	83.3
" " "	71	165.7	66.6
Barley-starch (paste)	65.5	168.6	52.4
Potato-starch (paste)	60	154.5	81.8
" " "	65.5	155.6	71.5
" " "	71	167.1	55.3

* The symbol R denotes the percentage of apparent maltose, determined by the cupric reduction method, on the dissolved matter in solution. The symbols $[\alpha]_{D^{20}}$ and R₈₈ indicate that the total solids have been calculated from the specific gravity of the solution by the divisor 3.93.

The very great differences between the constants yielded by the starch mashes and the starch paste conversions are apparent. It is also to be noted that the starches from different barleys give different constants, and the author hopes to continue his work in this direction. He brings forward evidence showing that in the process of mashing, as conducted in breweries, the starch granules are dissolved directly by the diastase and are not gelatinised prior to hydrolysis, as it is usually stated they are. It is probable

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

that the products formed in these starch mashes are different from those resulting from the hydrolysis of starch paste; and it is hoped that a study of the former may yield results of importance, both theoretically and practically.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 160).

CHAPTER III.

RADIATION OF THE NEW RADIO-ACTIVE SUBSTANCES.

Methods of Investigation of the Radiation.

In order to investigate the radiation emitted by radio-active bodies, any one of the properties of this radiation can be utilised. Thus the action of the rays on photographic plates may serve, or their property of ionisation of the air, which renders it a conductor, or their capacity for causing fluorescence of certain bodies. Henceforth, in speaking of these different methods of working, I shall use the expressions radiographic method, electrical method, fluoroscopic method.

The first two have been used from the beginning in the study of uranium rays; the fluoroscopic method can only be applied in the case of the new bodies which are strongly radio-active, for the feebly active bodies such as uranium and thorium produce no appreciable fluorescence. The electrical method is the only one which serves for exact determinations of intensity; the other two are specially adapted for giving qualitative results, and only furnish rough approximations. The results obtained with the three methods just considered are not strictly comparable the one with the other. The sensitive plate, the gas which is ionised, the fluorescent screen, are in reality receivers, which absorb the energy of the radiation, and transform it into another kind of energy, chemical energy, ionic energy, or luminous energy. Each receiver absorbs a fraction of the radiation, which depends essentially upon its nature. Later on, we shall see that the radiation is complex, that the fractions of the radiation absorbed by the different receivers may differ among themselves both quantitatively and qualitatively. Finally, it is neither evident, nor even probable, that the energy absorbed is entirely transformed by the receiver into the form that we wish for observation; part of this energy may be transformed into heat, into the evolution of secondary radiations which may or may not assist in the production of the observed phenomenon, into chemical action which differs from that under observation, &c., and here also the effective action of the receiver, with reference to the end we have in view, depends essentially upon the nature of that receiver.

Let us compare two radio-active substances, one containing radium and the other polonium, and which show an equal degree of activity in the condenser of Fig. 1. If each is covered with a thin leaf of aluminium, the second appears considerably less active than the first, and the same is the case when they are placed under the same fluorescent screen, if the latter is of sufficient thickness, or is placed at a certain distance from the two radio-active bodies.

Energy of Radiation.

Whatever be the method of research employed, the energy of radiation of the new radio-active substances is always found to be considerably greater than that of uranium and thorium. Thus it is that, at a short distance, they act instantaneously upon a photographic plate, whereas an exposure of twenty-four hours is necessary when operating with uranium and thorium. A fluorescent screen is vividly illuminated by contact with the new radio-active bodies, whilst no trace of luminosity is visible with uranium and thorium. Finally, the ionising action upon air is considerably stronger in the ratio of 10³ approximately.

But it is, strictly speaking, not possible to estimate the *total intensity of the radiation*, as in the case of uranium, by the electrical method described at the beginning (Fig. 1). With uranium, for example, the radiation is almost completely absorbed by the layer of air between the plates, and the limiting current is reached at a tension of 100 volts. But the case is different for strongly radio-active bodies. One portion of the radiation of radium consists of very penetrating rays, which penetrate the condenser and the metallic plates, and are not utilised in ionising the air between the plates. Further, the limiting current cannot always be obtained for the tensions supplied; for example, with very active polonium the current remains proportional to the tension between 100 and 500 volts. Therefore the experimental conditions which give a simple interpretation are not realised, and, consequently, the numbers obtained cannot be taken as representing the measurement of the total radiation; they merely point to a rough approximation.

Complex Nature of the Radiation.

The researches of various physicists (M^m. Becquerel, Meyer and von Schweidler, Giesel, Villard, Rutherford, M. and M^{me}. Curie) have proved the complex nature of the radiation of radio-active bodies. It will be convenient to specify three kinds of rays, which I shall denote, according to the notation adopted by Mr. Rutherford, by the letters α , β , γ .

I. The α -rays are very slightly penetrating, and appear to constitute the principal part of the radiation. These rays are characterised by the laws by which they are absorbed by matter. The magnetic field acts very slightly upon them, and they were formerly thought to be quite unaffected by the action of this field. However, in a strong magnetic field, the α -rays are slightly deflected; the deflection is caused in the same manner as with cathode rays, but the direction of the deflection is reversed; it is the same as for the canal rays of the Crookes tubes.

II. The β -rays are less absorbable as a whole than the preceding ones. They are deflected by a magnetic field in the same manner and direction as cathode rays.

III. The γ -rays are penetrating rays, unaffected by the magnetic field, and comparable to Röntgen rays.

Consider the following imaginary experiment:—Some radium, κ , is placed at the bottom of a small deep cavity, hollowed in a block of lead, ρ (Fig. 4). A sheaf of rays,

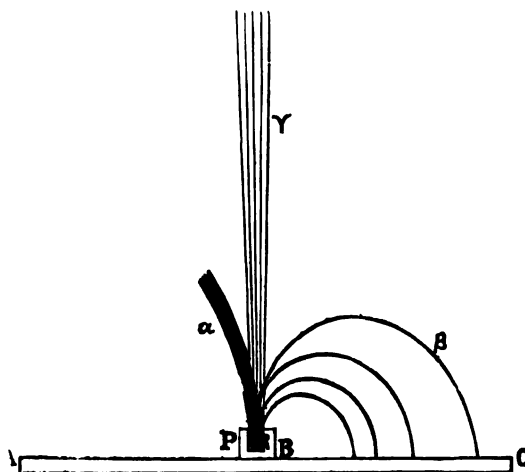


FIG. 4.

rectilinear and slightly expanded, streams from the receptacle. Let us suppose that a strong uniform magnetic field is established in the neighbourhood of the receptacle, normal to the plane of the figure and directed towards the back. The three groups of rays, α , β , γ , will now be separated.

* Thesis presented to the Faculté des Sciences de Paris

Then rather faint γ -rays continue in their straight path without a trace of deviation. The β -rays are deflected in the manner of cathode rays, and describe circular paths in the plane of the figure. If the receptacle is placed on a photographic plate, A C, the portion, B C, of the plate which receives the β -rays is acted upon. Lastly, the α -rays form a very intense shaft which is slightly deflected, and which is soon absorbed by the air. These rays describe in the plane of the figure a path of great curvature, the direction of the deflection being the reverse of that with the β -rays.

If the receptacle is covered with a thin sheet of aluminium (0.1 m.m. thick), the α -rays are suppressed almost entirely, the β -rays are lessened, and the γ -rays do not appear to be absorbed to any great extent.

Action of the Magnetic Field.

We have seen that the rays emitted by radio-active bodies have many properties common to cathode rays and to Röntgen rays. Cathode rays, as well as Röntgen rays, ionise the air, act on photographic plates, cause fluorescence, undergo no regular reflection. But the cathode rays differ from Röntgen rays in being deflected from their rectilinear path by the action of the magnetic field, and in the transportation of charges of negative electricity.

The fact that the magnetic field acts upon the rays emitted by radio-active substances was discovered almost simultaneously by MM. Giesel, Meyer and von Schweidler, and Becquerel. These physicists observed that the rays of radio-active substances are deflected by the magnetic field in the same manner and direction as the cathode rays; their observations were in relation to the β -rays.

M. Curie demonstrated that the radiation of radium comprises two groups of quite distinct rays, of which one is readily deflected by the magnetic field (β -rays), whilst the other seems to be unaffected by the action of this field (α - and γ -rays).

M. Becquerel did not find that the specimens of polonium prepared by us emitted rays of the cathode kind. On the contrary, he first noticed the effect of the magnetic field on a specimen of polonium prepared by himself. None of the polonium prepared by us ever gave rise to rays of the cathode order.

The polonium of M. Giesel only gives rise to these rays when recently prepared, and it is probable that the emission is due to the phenomenon of induced radio-activity of which we shall speak later.

The following are experiments which prove that one portion of the radiation of radium, and one portion only, consists of easily deflected rays (β -rays). These experiments were done according to the electrical method.

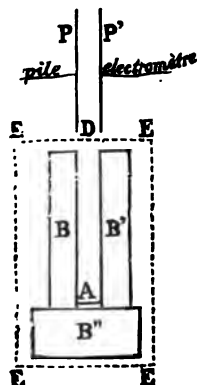


FIG. 5.

The radio-active body A (Fig. 5) sends forth radiations in the direction A D between the plates P and P'. The plate P is now at a potential of 500 volts, plate P' is connected to an electrometer and to a quartz electric piezometer. The

intensity of the current passing through the air under the influence of the radiations is measured. The magnetic field can be established at will perpendicular to the plane of the figure over the whole region E E E E. If the rays are deflected, even slightly, they no longer pass between the plates, and the current is suppressed. The region of the passage of the rays is surrounded with masses of lead, B, B', B'', and by the armatures of the electro-magnet; when the rays are deflected, they are absorbed by the masses of lead B and B'.

The results obtained depend essentially on the distance, A D, of the radiating substance, A, from the the condenser at D. If the distance A D is great enough (greater than 7 c.m.), most of the radium rays (90 to 100 per cent) arriving at the condenser are deflected and suppressed for a field of 2500 units. These are the β -rays. If the distance A D is less than 65 m.m., a smaller part of the rays are deflected by the action of the field; this portion is also entirely deflected by a field of 2500 units, and the proportion of the rays suppressed is not increased by increasing the field from 2500 to 7000 units.

The proportion of the rays not suppressed by the field increases with decrease of the distance, A D, between the radiating body and the condenser. For small distances, the rays which can be easily deflected form a very small fraction of the total radiation. The penetrating rays are therefore, for the most part, deviable rays of the cathode order (β -rays).

Under the experimental conditions just described, the action of the magnetic field on the α rays could not be well observed for the fields employed. The chief radiation, apparently undergoing no deflection, observed at a short distance from the radiating source, consisted of α -rays; the undeflected radiation observed at a greater distance consisted of γ -rays.

If an absorbing lamina (aluminium or black paper) is placed in the path of the bundle of rays, those which pass through are nearly all deflected by the field in such a way that, with the aid of the screen and the magnetic field, almost all the radiation is suppressed in the condenser, the remainder being due to the γ -rays, the proportion of which is small. The α -rays are absorbed by the screen.

An aluminium plate of $\frac{1}{16}$ m.m. thickness is sufficient for the suppression of almost all the rays not readily deflected when the substance is far enough from the condenser; for smaller distances (34 m.m. and 51 m.m.) two pieces of this aluminium foil are necessary to give the same result.

Similar determinations were made with four substances containing radium (chlorides or carbonates) of very different activity; analogous results were obtained.

It may be remarked that, in all cases, the penetrating rays deflected by the magnet (β -rays) form only a small fraction of the total radiation; they influence but slightly the determinations in which the whole radiation is made use of to produce conductivity of the air.

The radiation emitted by polonium may be studied by the electrical method. When the distance, A D, of the polonium from the condenser is varied, no current is observed at first while the distance is fairly great; on nearing the polonium, the radiation suddenly becomes manifest with great intensity; the current then increases uniformly whilst approaching the polonium, but the magnetic field produces no appreciable effect under these conditions. The radiation of polonium is apparently limited in space, and does not pass into the air beyond a kind of sheath surrounding the substance to a thickness of several centimetres.

The interpretation of the experiments I have just described must be accompanied by some important general reservations. In speaking of the proportion of the rays deflected by the magnet, I refer only to that portion of the radiation capable of causing a current in the condenser. In employing the fluorescent action of the Becquerel rays, or their action on photographic plates, the proportion would probably be different—a measure of intensity having, as a rule, no meaning except for the method of measurement adopted.

The rays of polonium are α -rays. In the experiments just described, I observed no action of the magnetic field upon them, but the experimental conditions were such that a slight deflection would pass unnoticed.

The experiments made by the radiographic method confirmed the preceding results. Taking radium as the source of radiation, and receiving the impression on a plate parallel to the primitive shaft and normal to the field, a very clear print is obtained of two shafts separated by the action of the field, the one deflected, the other not deflected. The β -rays constitute the deflected beam; the α -rays, being very slightly deflected, are not to be distinguished from the undeflected bundle of the γ -rays.

(To be continued).

NOTES ON THE COMPOSITION OF SOME ANCIENT SLAG.

By A. W. COMBER, A.I.C., F.C.S.

A YEAR or two ago, when on the Island of Elba—famed for its iron ores as well as its Napoleonic associations—I was asked to make some analyses of samples of ancient slag.

That the Elban ore was worked by the Romans, and probably by the Greeks, is a well-assured fact, borne out by more than one reference in the classics, and the slag in question, of which considerable quantities are found on the island, exists to-day as an interesting evidence of those early metallurgical operations.

I made two analyses of this slag, the results of which are herewith appended. The first sample (a) consisted of only one piece, while of (b) I was supplied with a considerable quantity, and, consequently, the latter should be taken as more truly representative of the general constitution of the slag.

	(a).	(b).
Silica	16.27	25.95
Ferric oxide (Fe_2O_3)	15.23	15.86
Ferrous oxide (FeO)	56.24	44.67
Oxide of aluminium	5.81	7.31
Oxide of manganese	0.47	0.40
Oxide of calcium	2.37	2.00
Oxide of magnesium	0.77	0.67
Phosphoric acid (P_2O_5)	0.156	0.232
Sulphuric acid (SO_3)	0.072	0.120
Arsenic acid (As_2O_3)	nil	nil
Water above 100°C	1.70	1.80
Water at 100°C	0.88	0.98
	99.968	99.992
	Per cent.	Per cent.
Metallic iron	54.41	45.84
Phosphorus	0.068	0.102
Sulphur	0.029	0.047

The results, apart from the high percentage of iron and the somewhat large quantity of phosphorus, do not call for special comment.

In considering the apparent waste of iron, it should be remembered, however, that apart from their extremely primitive plant, these ancient workers, by reason of the small quantity of ore operated upon, were able to carefully select their material, utilising only such pieces of ore as were apparently of the highest grade.

To illustrate this, I give an analysis of a selected sample of Elban ore which I made a few months previously:—

	Ore dried at 100°C .
	Per cent.
Iron	68.89
Phosphorus	trace
Sulphur	nil
Silica	trace

This of course hardly explains the high phosphorus result in the slag, which, however, may have been caused by other means, but it is sufficient to indicate that, if judiciously selected, ore of exceptionally high quality was at hand to be utilised. I might here mention that during my stay in Elba the ore exported averaged considerably over 60 per cent of iron, the analyses being made on samples dried at 100°C .

Assuming, therefore, the ore taken for smelting to have contained 65 per cent of iron, one can readily see that a fair margin for extraction is left, even when the metal remaining amounts to nearly one-half of the slag, especially if one considers the matter from the standpoint of the old-time metallurgist to whom time was no object, neither was he so circumstanced that the cost of production had to be calculated out to the fraction of a denarius!

Ramabudrapur, India.

NOTICES OF BOOKS

Practical Electro-Chemistry. By BERTRAM BLOUNT, F.I.C., F.C.S., Assoc.Inst.C.E. Second Impression. Westminster: Archibald Constable and Co., Ltd. New York: The Macmillan Company. 1903.

THE title of this book, the success of which has been great enough to warrant the production of a second impression, is perhaps somewhat misleading; it does not contain descriptions of experiments with directions for their performance, but gives an account of the practice of electro-chemistry as applied to manufacture and commercial processes. The subjects dealt with include the winning and refining of metals and their alloys by electrolytic methods, electro-deposition, and the manufacture of organic compounds and fine chemicals. The author has very wisely omitted historical matter, which has by no means diminished the value of the book for all practical purposes, while increasing the space available for the consideration of details as to expense and cost of working; the three years which have elapsed since the first appearance of the book have in many cases considerably affected the magnitude of these values, which were perhaps sometimes rather over estimated originally, as in the case of aluminium, but on the whole the statements will be found trustworthy. A few comparatively unimportant misprints are scattered through the book, and some omissions are noticeable; for example, no mention is made of the preparation of the metals of the alkaline earths by the electrolysis of the fused chlorides which has been effected by a special process said to be applicable on a large scale. But on the whole the treatment of the subject is most practical and efficient, and the book will be found quite indispensable by the student of electro-chemistry.

Elektro-metallurgie des Nickels. ("The Electro-metallurgy of Nickel.") By Dr. W. BORCHERS. Halle-a-S.: Wilhelm Knapp. 1903.

THE details of the processes of nickel refining and plating as actually employed commercially are very little known, though great activity has been displayed by many workers in the investigation of the chemical and physical facts which underlie their successful performance. This monograph therefore, while it does not reveal the special methods adopted by the largest and most important firms, does much to supply a want in collecting and editing the copious accounts of researches of the electro-chemical treatment of crude nickel, and abstracting patent specifications. As a compilation of this sort it will be found an excellent example of judicious selection, though perhaps a rather undue prominence is given to the description of old methods which, although interesting from the point of view of the development of present processes, have long since ceased to be of any practical value whatever. The author

deals first with the treatment of crude cast nickel without reference to the separation of the metal from copper, and then proceeds to the special means of obtaining chemically pure nickel, and the processes used for the electrolytic deposition of the metal. Mond's method of volatilisation and decomposition of nickel carbonyl is dismissed with a very brief description, amounting to a few lines only.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.

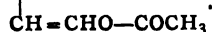
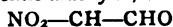
Series 3, Vol. xxix., No. 7.

Separation and Estimation of Antimony by Electrolysis.—A. Hollard.—Already inserted in full.

Separation and Estimation of Zinc by Electrolysis.—A. Hollard.—Already inserted in full.

Sulphurised and Azotised Derivatives of Sulphide of Carbon. (X.). Thermochemistry.—Marcel Delépine.—The author burnt, in a Berthelot calorimetric bomb, some of the principal substances used in his research on the sulphurised and azotised derivatives of sulphide of carbon, as well as some others belonging to another order, but having some isomeric relations with them. The results obtained are given in a table, and some interesting conclusions may be drawn therefrom.

The Nitration of Furfurane. (I.).—R. Marquis.—The author has effected the nitration of furfuran in solution in acetic anhydride. Under these conditions he did not immediately obtain nitrofurfurane, but a special reaction took place which caused the break-up of the furfuranic radical and the formation of a derivative of succinic aldehyde. This liquid, nitrated derivative, insoluble in water, is remarkably unstable; it decomposes, sometimes spontaneously, giving off nitrous fumes and leaving a voluminous residue of carbon. Two special reactions have enabled the author to establish its constitution. Decomposition by means of water gives rise to the formation of nitrous acid, acetic acid, and fumaric aldehyde. The formation of fumaric aldehyde is again shown by another reaction. When the derived nitrated liquid is treated with hydrazine, orthodiazine can be isolated from the product of the reaction. Now this base may be considered as the aldazine of fumaric aldehyde. The preceding reactions give to this nitrated derivative the constitution of an acetylated derivative of nitrosuccinic aldehyde, with the formula—



The Nitration of Furfurane. (II.). β -Nitrofurfurane and Dinitrofurfurane.—R. Marquis.—After some experiments the author adopted the following method for the nitration of furfuran:—For 1 part of furfuran he used 5 parts of fuming nitric acid added drop by drop, and 8 parts of acetic anhydride cooled in ice and salt. When all the furfuran has been added, the mixture is thrown on to broken ice, and exhausted three or four times with ether. The ethereal solution is washed with a solution of bicarbonate of soda until no longer acid, then with water. The solution is then dried over anhydrous sulphate of soda, and distilled on the water-bath until about three-quarters of the ether is driven off; the remainder is removed *in vacuo* in the cold. The residue, which is a thick yellow liquid, insoluble in water, is nitrosuccinic acetone. This liquid is treated with pyridine, and the excess distilled off *in vacuo* on the water-bath. The residue is carried over by the steam, and an oily liquid appears in the condenser; it solidifies in the flask, and consists of the nitro-furfurane sought for. This nitrofurfurane is purified by crystallisation in petroleum ether, and when treated with boiling

nitric acid of 1.2 density, it is transformed into a dinitrated derivative. This substance is identical with the dinitrofurfurane obtained by Messrs Hill and White (*Am. Chem. Journ.*, vol. x., p. 380), by treating sulphopyromucic acid with nitric acid.

Estimation of Vanilline in Vanillas.—A. Moulin.—While working on the colorimetric estimation of dulcine, the author came across an intense colouration which was recognised as being due to the presence of vanilline. The vanilline was eliminated by means of an excess of bisulphite of sodium, and an attempt made to apply the colorimetric method to the estimation of this substance. The principle of the method adopted was as follows:—If vanilline, $\text{C}_6\text{H}_3\begin{matrix} \text{OCH}_3 \\ | \\ \text{OH} \\ | \\ \text{CHO} \end{matrix}$, in which the group $\text{C}_6\text{H}_3\text{—O—CH}_3$ is

found, is treated with fuming nitric acid, this group passes to the state of picrate of methyl, the solution of which is characterised by the yellow tint of the picric compounds, and serves for the estimation of the vanilline by comparison with a titrated colour scale.

Method of Estimating Glycerin in Wine.—A. Trillat.—Already noticed.

The Entanglement of Glycerin by Water-vapour. Maurice Nicloux.—The distillation of glycerin by means of steam, either *in vacuo* or superheated, offers several disadvantages. The author has devised a new apparatus for this distillation, and describes it fully. The following are some of the results obtained:—

Glycerin used.	Volume of liquid carried over.	Glycerin recovered.
M.grm.	C.c.	M.grm.
10.2	120	9.8
25.6	180	25.5
43.0	260	44.1
76.9	320	76.0
102.5	514	101.0

Composition of Sheep's Milk.—MM. Trillat and Forestier.—Analyses were made of 171 samples of sheep's milk, of which 37 are given here in full. The extract was taken by evaporating 10 c.c. of the milk for seven hours on the water-bath, in a platinum crucible 7 c.m. in diameter. The sugar was estimated on 10 c.c. of liquid; the lactose was titrated by Fehling's solution. The butter was obtained by treating the coagulum with ether, and weighing the portion extracted; the casein was estimated by difference. The figures given are somewhat higher than those found by other analysts. It is interesting to observe that the weight of the extract is often as high as 200 grms. per litre of sheep's milk, while in the case of cow's milk it is rarely more than 150 to 160 grms. The ash, generally about 9 grms., shows that sheep's milk is more highly mineralised than cow's milk.

MISCELLANEOUS.

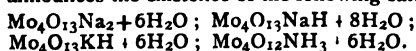
Announcement.—Messrs. Gurney and Jackson will issue before the end of October Volume I., containing Parts I. and II., of the third and greatly enlarged edition of Dr. George Lunge's "Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali."

The Action of Organic Acids on Metallic Antimony.—B. Moritz and C. Schneider.—Observation has shown that finely divided metallic antimony is soluble in the presence of air, in aqueous solutions of certain organic acids, and of their acid salts. The authors establish first of all, by measurements made with solutions of citric or lactic acid partially saturated with carbonate of soda, the essential rôle played by the oxygen of the air; solution does not take place in an inert atmosphere. The amount of oxygen absorbed for each atom of antimony dissolved corresponds to the formation of the oxide, Sb_2O_3 . The amount of antimony dissolved, in the presence of an excess of air, increases first with the amount of alkaline carbonate

introduced into the solution, reaches a maximum, and then decreases if we continue to add more carbonate of soda. The amount corresponding to the maximum action is lower than that which would be necessary for the formation of a neutral salt of sodium and antimonyl. The authors then looked for the organic acids capable of dissolving antimony under these conditions. The simple acids of the fatty series, saturated or non-saturated, are without action. On the other hand, the monobasic acid alcohols (glycolic, lactic, α -oxybutyric, β -oxybutyric, oxyisobutyric), give rise to the phenomena in a most distinct manner. It is the same with oxalic acid, but not with malonic, succinic, malic, tartaric, and citric. Thus we see that the property of dissolving antimony in the presence of air is almost entirely limited to the acid alcohols.—*Zeit. Physik. Ch.*, vol. xli., p. 129.

Reaction between Persulphate of Potassium and Hydriodic and Phosphorous Acids; an Example of Catalysis by Transport.—Wilhelm Federlin.—Persulphate of potassium only oxidises phosphorous acid very slowly, while it rapidly transforms hydriodic acid into iodine; on the other hand, iodine rapidly oxidises phosphorous acid. The addition of hydriodic acid to a mixture of persulphate and phosphorous acid thus accelerates the reaction of these two bodies one on the other; in this manner, the hydriodic acid would play the part, in this reaction, of a catalyser by transport. The examination made by the author of the total speed of the reaction, as well as of those of the two simple reactions, of which it is the result, shows that if we put on one side the interference caused by the presence of PO_3H_3 in the reaction of $\text{S}_2\text{O}_8\text{K}_2$ on KI, and also take note of the incorrectness of the mathematical formula used, there is sufficient concordance between the speed observed and the speed calculated from the speeds of the component reactions. These latter therefore have not any particular influence on each other. Iron and copper, which accelerate the reaction of $\text{S}_2\text{O}_8\text{K}_2$ on KI, have a more feeble catalytic action in the presence of PO_3H_3 , perhaps because they are fixed by this acid, or by the phosphoric acid resulting from its oxidation.—*Zeit. Physik. Ch.*, vol. xli., p. 565.

Molybdc Acid.—F. Mylius.—There is no hydrate of molybdc acid corresponding to orthotelluric acid, $\text{Te}(\text{OH})_6$, the white milky precipitates of molybdc acid are badly defined. The colourless molybdc acid in aqueous solution corresponds in its properties generally with allotelluric acid. On the other hand, there is a yellow molybdc acid, $(\text{MoO}_3\text{H}_4)_x$, which is formed slowly by the action of nitric or hydrochloric acid on solutions of the alkaline molybdates, or of white molybdc acid. An acid molybdate of ammonium, $\text{NH}_3\cdot 4\text{MoO}_3\cdot 6\text{H}_2\text{O}$, has been prepared which, on being heated, first loses half its ammonia and its water; if heated more strongly, the residue becomes green as a result of reduction. This salt is deposited in small colourless needles by the addition of NO_3H , HCl , or SO_4H_2 in quantities calculated from the solution of ordinary molybdate of ammonia; the white cheesy molybdc acid is first formed, and this becomes gradually changed. This salt is slightly soluble in cold water, easily soluble in hot water, but at about 60° the solution changes, giving a deposit of a less hydrated insoluble salt. It has a very acid reaction, and decomposes the carbonates. It precipitates albumin; its solution is not precipitated immediately by nitric acid; eventually it forms still more acid salts, or the yellow acid. The author further announces the existence of the following salts:—



—*Berichte*, vol. xxxvi., p. 638.

Sesquisulphide of Phosphorus.—J. Mai and F. Schaffer.—With the object of examining some of the properties of, and the conditions under which commercial sesquisulphide of phosphorus, used for the manufacture of matches, undergoes change, the authors heated some of this substance to 180° for some hours in a current of car-

bonic acid; a little phosphoretted hydrogen was given off (resulting from a trace of PO_3H_3), as well as fumes, luminous in the dark, and a slight yellow sublimate; these two latter occurrences are due to the distillation of P_2S_5 . If we commence with P_2S_5 , re-crystallised in sulphide of carbon or in a hydrocarburised solvent, the same phenomena occur, with the exception of the formation of the phosphoretted hydrogen. When heated in the air for some time at about 40 – 50° the P_2S_5 changes by slow oxidation, becomes luminous in the dark, and is converted into a pitchy mass with a strongly acid reaction. When heated in a current of steam, the P_2S_5 is carried off, giving a white deposit formed principally of P_2S_5 , with products of its oxidation. The fumes are luminous in the dark, like phosphorus in Mitscherlich's experiment; however, to a trained eye the phosphorescent appearance is slightly different. Finally, above 350° , in a current of carbonic acid, the P_2S_5 changes rapidly, furnishing considerable quantities of red phosphorus.—*Berichte*, vol. xxxvi., p. 870.

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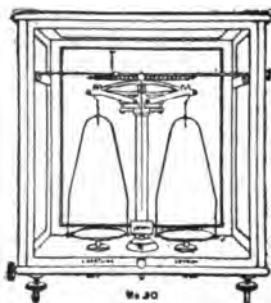
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2289.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 171).

CHAPTER III. (continued).

Deflected β -Rays.

THE experiments of M. Giesel and M^m. Meyer and von Schweidler showed that the radiation of the radio-active bodies is in part, at least, deflected by a magnetic field, and that this deflection resembles that of the cathode rays. M. Becquerel investigated the action of the field on the rays by the radiographic method. The experimental arrangement was that of Fig. 4. The radium was placed in the lead receptacle P, and this receptacle was placed on the sensitive face of a photographic plate, A C, covered with

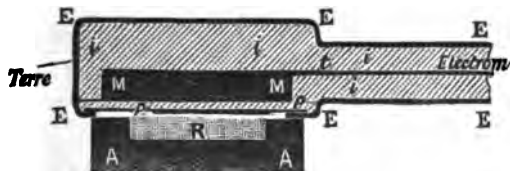


FIG. 6.

black paper. The whole was placed between the poles of an electro-magnet, the magnetic field being normal to the plane of the figure.

If the field is directed to the back of this plane, the part, B C, of the plate is acted upon by rays which, after having

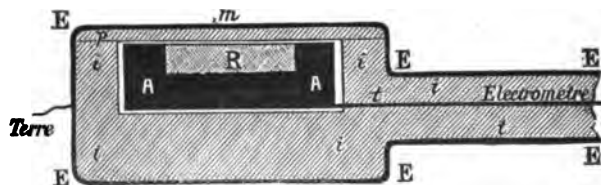


FIG. 7.

described circular paths, return to the plate and strike it at a right angle. These rays are β -rays.

M. Becquerel has demonstrated that the impression consists of a wide diffused band, a continuous spectrum indeed, showing that the sheaf of deviable rays emitted by the source is formed of an infinite number of radiations unequally deflected. If the gelatin of the plate be covered with different absorbent screens (paper, glass, metals), one portion of the spectrum is suppressed, and it is found that the rays most deflected by the magnetic field—otherwise those which have the smallest radius of curvature—are the most completely absorbed. With each screen, the impression on the plate begins at a certain distance from the source of radiation, this distance being proportional to the absorptive power of the screen.

Charge of the Deflected Rays.

The cathode rays are, as shown by M. Perrin, charged with negative electricity. Further, according to the experiments of M. Perrin and M. Lenard, they are capable of carrying their charge through the metallic envelopes con-

nected to earth and through isolating screens. At every point where the cathode rays are absorbed, there is a continuous evolution of negative electricity. We have proved that the same is the case for the deflected β -rays of radium. *The deviable β -rays of radium are charged with negative electricity.*

(NOTE.—Let the radio-active substance be placed on one of the plates of a condenser, this plate being connected to earth; the second plate is connected to an electrometer, it receives and absorbs the rays emitted by the substance. If the rays are charged, a continuous flow of electricity into the electrometer should be observed. In this experiment, carried out in air, we were not able to detect a charge accompanying the rays, but such an experiment is not delicate. The air between the plates being caused by the rays to conduct, the electrometer is no longer isolated, and can only respond to charges if these be sufficiently strong. In order that the α -rays may not interfere with the experiment, they may be suppressed by covering the source of radiation with a thin metallic screen. We repeated this experiment, without more success, by causing the rays to pass through the interior of a Faraday cylinder in connection with the electrometer).

According to the preceding experiments, it was evident that the charge of the rays of the radiating body employed was a weak one.

In order to fix a feeble evolution of electricity upon the conductor which absorbs the rays, this conductor should be completely insulated; this is effected by screening it from the air, either by placing it in a tube with a very perfect vacuum, or by surrounding it with a good solid dielectric. We employed the latter arrangement.

A conducting disc, m m (Fig. 6), is connected by the wire, t, to the electrometer; the disc and wire are completely enveloped by the insulating substance p p; the whole is again surrounded with the metallic covering, e e e e, which is in electric connection with the earth. The insulator, p p, and the metallic envelope are very thin upon one of the faces of the disc. This face is exposed to the radiation of the barium and radium salt, R, placed outside

in a lead receptacle. The rays emitted by the radium penetrate the metallic envelope and the insulating lamina, p p, and are absorbed by the metallic disc, m m. The latter then becomes the source of a continuous evolution of negative electricity, as determined by the electrometer, and is measured by means of a quartz piezometer.

The current thus created is very weak. With very active barium-radium chloride, forming a layer of 2.5 sq. c.m. in area, and of 0.2 c.m. in thickness, a current of magnitude 10^{-11} ampères is obtained, the rays utilised having traversed, before being absorbed by the disc m m, a thickness of aluminium of 0.01 m.m., and a thickness of ebonite of 0.3 m.m.

We used successively lead, copper, and zinc for the disc m m, ebonite and paraffin for the insulator; the results obtained were the same.

The current diminishes with increasing distance from the source of radiation, R, also when a less active product is used.

We obtained the same results again when the disc m m is replaced by a Faraday cylinder filled with air, and covered outside with insulating material. The opening of the

* Thesis presented to the Faculté des Sciences de Paris.

cylinder, closed by the thin insulating plate, $p\beta$, was opposite the radiating source.

Finally, we made the inverse experiment, which was to place the lead receptacle with the radium in the centre of the insulating material and in connection with the electrometer (Fig. 7), the whole being surrounded with the metallic covering connected to earth.

Under these conditions, it is evident from the electrometer that the radium has a positive charge equal in magnitude to the negative charge of the former experiment. The radium rays penetrate the thin dielectric plate, $p\beta$, and leave the conductor inside carrying with them negative electricity.

The α -rays of radium do not interfere in these experiments, being almost completely absorbed by a very thin layer of matter. The method just described is not suitable for the study of the charge of the rays of polonium, these rays very slightly penetrating. We observed no indication of any charge in the case of polonium, which gives rise to α -rays only; but, for the reason just given, no conclusion can be drawn from this.

Thus, in the case of the deflected β -rays of radium, as in the case of cathode rays, the rays carry a charge of electricity. But, hitherto, the existence of electric charges uncombined with matter has been unknown. In the study of the emission of the β -rays of radium, we are therefore led to make use of the theory which is in vogue for the study of cathode rays. In this ballistic theory, formulated by Sir William Crookes, since developed and completed by Prof. J. J. Thomson, the cathode rays consist of extremely minute particles, which are hurled from the cathode with great velocity, and which are charged with negative electricity. We might similarly conceive that radium sends into space negatively electrified particles.

A specimen of radium, enclosed in a solid thin perfectly insulated envelope, should become spontaneously charged to a very high potential. By the ballistic hypothesis the potential would increase until the potential difference of the surrounding conductors became sufficient to hinder the ejection of the electrified particles and to cause their return to the source of radiation.

We have performed an experiment on these lines. A specimen of very active radium was enclosed for some time in a glass vessel. In order to open the vessel, we made a trace on the glass with a glass cutter. Whilst so doing, we clearly heard the report of a spark, and upon examining the vessel with a magnifying glass, we observed that the glass had been pierced by a spark at the spot where it had been weakened by the scratch. The phenomenon produced is comparable to the rupture of the glass of an over-charged Leyden jar.

The same phenomenon occurred with another glass. Further, at the moment of the passing of the spark, M. Curie, who was holding the glass, felt the electric shock of discharge in his fingers.

Certain kinds of glass have good insulating properties. If the radium is enclosed in a sealed glass vessel, well insulated, it is to be expected that, at a given moment, the vessel will be spontaneously perforated.

Radium is the first example of a body which is spontaneously charged with electricity.

Action of the Electric Field upon the Deflected β -Rays of Radium.

The β -rays of radium, being analogous to the cathode rays, should be deflected by an electric field in a manner similar to the latter; i.e., as would a particle of matter negatively charged and hurled into space with a great velocity. The existence of such a deflection has been demonstrated both by M. Dorn and M. Becquerel.

Let us consider the case of a ray which traverses the space situated between the two plates of a condenser. Suppose the direction of the ray parallel to the plates: when an electric field is established between the latter, the ray is subjected to the action of this uniform field along its whole path in the condenser l . By reason of this action the ray

is deflected towards the positive plate and describes the arc of a parabola; on leaving the field, it continues its path in a straight line, following the tangent to the arc of the parabola at the point of exit. The ray can be received on a photographic plate perpendicular to its original direction. Observations are taken of the impression produced on the plate when the field is zero, and when it has a known value, and from that is deduced the value of the deflection, δ , which is the distance of the points in which the new direction of the ray and its original direction meet a common plane perpendicular to the original direction. If h is the distance of this plane from the condenser, i.e., at the edge of the field, we have, by a simple calculation,—

$$\delta = \frac{eFl\left(\frac{l}{2} + h\right)}{mv^2};$$

m being the mass of the moving particles, e its charge, v its velocity, and F the strength of the field.

The experiments of M. Becquerel enable him to assign a value approaching to δ .

Relation of the Charge to the Mass for a Particle Negatively Charged emitted by Radium.

When a material particle having a mass m and a negative charge e , is projected with a velocity v into a uniform magnetic field perpendicular to its initial velocity, this particle describes, in a plane normal to the field and passing through its initial velocity, an arc of a circle of radius ρ , so that— H being the strength of the field—we have the relation—

$$H\rho = \frac{mv}{e}.$$

If, for the same ray, the deflection, δ , and the radius of curvature, ρ , be measured in a magnetic field, values could be found from these two experiments for the ratio $\frac{e}{m}$ and for the velocity, v .

The experiments of M. Becquerel threw the first light upon this subject. They gave for the ratio $\frac{e}{m}$ a value

approximately equal to 10^7 absolute electro-magnetic units, and for v a magnitude 1.6×10^{10} . These values are of the same order of magnitude as those of the cathode rays.

Accurate experiments have been made upon the same subject by M. Kaufmann. This physicist subjected a narrow beam of radium rays to the simultaneous action of an electric field and a magnetic field, the two fields being uniform and having a similar direction, normal to the original direction of the beam. The impression produced on a plate normal to the primitive beam and placed beyond the limits of the field with reference to the source, has the form of a curve, each point of which corresponds to one of the rays of the original beam. The most penetrating and least deflected rays are at the same time those with the greatest velocity.

It follows from the experiments of M. Kaufmann that, for the radium rays, of which the velocity is considerably greater than that of the cathode rays, the ratio $\frac{e}{m}$ decreases, while the velocity increases.

According to the researches of J. J. Thomson and Townsend, we may assume that the moving particle, which constitutes the ray, possesses a charge, e , equal to that carried by an atom of hydrogen during electrolysis, this charge being the same for all the rays. We are therefore led to the conclusion that the mass of the particle, m , increases with increase of velocity.

These theoretical considerations lead to the idea that the inertia of the particle is due to its state of charge during motion, the velocity of an electric charge in motion being incapable of modification without expenditure of energy. To state it otherwise, the inertia of the particle is of electro-magnetic origin, and the mass of the particle is—in part at least—a virtual mass or an

electro-magnetic mass. M. Abraham goes further, and assumes that the mass of the particle is entirely an electro-magnetic mass. If, according to this hypothesis, the value of this mass, m , be calculated for a known velocity, v , we find that m approaches infinity when v approaches the velocity of light, and that m approaches a constant value when the velocity, v , is much less than that of light. The experiments of M. Kaufmann are in agreement with the results of this theory, the importance of which is great because it foreshadows the possibility of establishing mechanical bases upon the dynamical of little particles of matter charged in a state of motion.

These are the figures obtained by M. Kaufmann for

$\frac{e}{m}$ and v .

$\frac{e}{m}$ Electro-magnetic units.	v c.m. sec.	
1.865×10^7	0.7×10^{10}	For cathode rays (Simon).
1.31 "	2.36 "	For radium rays (Kaufmann).
1.17 "	2.48 "	
0.97 "	2.59 "	
0.77 "	2.72 "	
0.63 "	2.83 "	

M. Kaufmann concludes, from comparison of his experiments with the theory, that the limiting value of the ratio $\frac{e}{m}$ for radium rays of relatively small velocity would be the same as the value $\frac{e}{m}$ for cathode rays.

The most complete experiments of M. Kaufmann were made with a minute quantity of pure radium chloride, with which we provided him.

According to M. Kaufmann's experiments, certain β -rays of radium possess a velocity very near to that of light. These rapid rays seem to possess great penetrating capacity towards matter.

Action of the Magnetic Field upon the α -Rays.

In a recent work, Mr. Rutherford announced that, in a powerful electric or magnetic field, the α -rays of radium are slightly deflected, in the manner of particles positively electrified and possessing great velocity. Mr. Rutherford concludes from his experiments that the velocity of the α -rays is of the order of magnitude 2.5×10^8 $\frac{\text{c.m.}}{\text{sec.}}$

and that the ratio $\frac{e}{m}$ for these rays is of the order of

magnitude 6×10^4 , which is 10^4 times as great as for the deflected β -rays. We shall see later that these conclusions of Mr. Rutherford are in agreement with the properties already known of the α -radiation, and that they account, in part at least, for the law of absorption of this radiation.

The experiments of Mr. Rutherford have been confirmed by M. Becquerel. M. Becquerel has further demonstrated that polonium rays behave in a magnetic field like the α -rays of radium, and that, for the same field, they seem to have the same curvature as the latter.

It also appears from M. Becquerel's experiments that the α -rays do not form a magnetic spectrum, but act rather like a homogeneous radiation, all the rays being equally deflected.

Action of the Magnetic Field on the Rays of other Radio-active Substances.

We have just seen that radium gives off α -rays comparable to the tube rays, β -rays comparable to cathode rays, and γ -rays which are penetrating and not deflected. Polonium gives off α -rays only. Amongst the other radio-active substances, actinium seems to behave like radium, but the study of its radiation has not yet advanced so far as in the case of radium. As regards the faintly radio-active bodies, we know to-day that uranium and thorium give rise to α -rays as well as β -rays (Becquerel, Rutherford).

(To be continued).

A NEW METHOD FOR THE DETECTION AND ESTIMATION OF THE MINUTEST TRACES OF ARSENIC.

By ARMAND GAUTIER.

DURING the course of my publications on the detection and estimation of small quantities of arsenic (*Comptes Rendus*, vol. lxxxi., p. 239; *Ann. Chim. Phys.*, Series 5, vol. viii., p. 384), especially when I wished to demonstrate the normal existence and the localisation of this metalloid in the organs of animals (*Comptes Rendus*, vol. cxxix., pp. 929 and 936; vol. cxxx., p. 284; vol. cxxxiv., p. 1394; *Bull. Soc. Chim.*, Series 3, vol. xxvii., pp. 135 and 833), I found it necessary to verify, first of all, the important point of knowing if the method of nitrosulphuric carbonisation that I had used since the year 1875, would enable me to collect the whole of the arsenic without any loss. More recently, I have shown that this method is sufficiently precise to enable two-thousandths, or even one-thousandth of a m.grm. of arsenic to be recovered from 100 grms. of animal or vegetable matter, without loss; that is, in 50 or 100 million times its weight of foreign organic matter (*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 639).

Thus it would not appear as if there was room to attempt to improve so exact a method. However, it is so delicate in its application, it requires the use of so many reagents (distilled water, sulphuric and nitric acids, sulphuretted hydrogen, ammonia, sulphurous acid, bisulphites, zinc, &c.), that there may be some room for doubt, when we are dealing with infinitesimal quantities of arsenic, the thousandth of a m.grm., and less, in comparatively large quantities of animal or vegetable matter. I shall show that distilled water, ammonia supposed to be pure, pure nitric acid, sulphurous acid, and, above all, sulphuretted hydrogen well washed with acids and water, always contain traces of arsenic. In the experiments I have just concluded, after the purification of all these reagents, the total amount of arsenic used in an experiment for its detection in 100 grms. of muscle or yolk of egg, was from one-half to three-quarters of a thousandth of a m.grm. of the metalloid.

Another reason has caused me to attempt to simplify my old method. It cannot be applied when it is a question of recovering the arsenic in substances very rich in soluble chlorides, such as sea-water, highly chlorised mineral waters, salt meats, kitchen salt, or in solutions too rich in iron, as will be seen later on. No matter what we do, the arsenic is partially lost in the above cases, either in the form of chloride, which escapes without being decomposed, even passing alkaline water, or in the state of sulpharsenate of iron.

The new method I am about to describe is of extreme simplicity and of remarkable accuracy. It can be used for the physiological determination of traces of arsenic as well as for expert legal work, but I will confine myself, for the time being, to a description of the method and the results obtained in cases where the old methods are inapplicable or uncertain.

This method is founded, in principle, on the well-known observation, that when arsenic exists, even in very small quantities, in the presence of iron in a potable or mineral water, the latter by oxidation and precipitation always carries with it a part or the whole of this arsenic.

My recent researches have shown that this property of iron is absolute, and that this entanglement of the arsenic by the ferric sub-salts is so complete, under the experimental conditions I adopted, that 1/1000th of a m.grm. of arsenic added in the form of arsenite or arsenate to a litre of pure water, or water containing sea-salt or other salts, was entirely removed by the iron, and could be estimated easily and directly by placing the precipitate re-dissolved in dilute sulphuric acid in the Marsh apparatus.

I prepare my reagent in the following manner:—100 grms. of commercial ferrous sulphate are dissolved in 500

grms. of distilled water, with the addition of 25 grms. of pure sulphuric acid, and treated with sulphuretted hydrogen. Boil and filter; then, while still warm, oxidise the ferrous salt by means of 28 grms. of nitric acid free from arsenic. The ferric hydrate is then precipitated by ammonia free from arsenic, and, after washing, the ferric hydrate is re-dissolved in cold, pure, dilute sulphuric acid. This ferric sulphate still contains appreciable traces of arsenic (0.002 to 0.003 m.grm. of arsenic in 3 grms. of Fe_2O_3). This is removed by digesting the ferric solution for two days with pure granulated zinc and then boiling *in vacuo* (P. Clausmann). The salt is then re-oxidised with a little nitric and sulphuric acids, and the ferric hydrate precipitated by a slight excess of pure ammonia, which re-dissolves the zinc. There now remains only to wash and to add pure, dilute, cold sulphuric acid to the ferric hydrate thus prepared. One hundred c.c. of this reagent containing 30 grms. of Fe_2O_3 per litre gave, by the method I am about to describe, a ring corresponding to less than half a thousandth of a m.grm. of arsenic. Five c.c. of this solution are sufficient to precipitate the arsenic in 300 or 400 c.c. of water, so it is obvious that only 0.0000025 m.grm. (practically none at all) of arsenic is introduced through this reagent. With this reagent the following observations can be made:—

If we take two litres of distilled water and evaporate them in the presence of 40 grms. of nitric acid and 10 grms. of sulphuric acid practically free from arsenic (they contain together less than 0.0001 m.grm. of arsenic), and after driving off the nitric acid, we dilute with water and pour the whole into the Marsh apparatus, we obtain:—

	Arsenic per litre. M.grm.
Water distilled in a tinned copper retort ..	0.0007
Water distilled in a glass retort, after adding 5 grms. per 1000 of pure CO_3Na_2 ..	0.0010

A litre of this slightly arsenical water is boiled after the addition of 5 c.c. of the above ferric solution; after cooling, it is saturated with pure ammonia, boiled again for a few moments, and then filtered. The solution evaporated in the presence of pure nitric and sulphuric acids is concentrated, heated to drive off the nitric acid, diluted with water, and placed in the Marsh apparatus. *It does not give any trace of arsenic.* (At least no appreciable trace; that is to say, a smaller quantity than 0.00033 m.grm. of arsenic).

To 2 litres of this water thus freed from arsenic, we add 0.002 m.grm. of arsenic in the form of arsenite of soda, then 5 c.c. of the ferric solution. Boil, make slightly alkaline, and collect the precipitate which is dissolved in a slight excess of sulphuric acid; the sulphate formed is poured directly into the Marsh apparatus. In this manner we found:—*Arsenic added to 2 litres of water, 0.002 m.grm.; arsenic found, 0.002 m.grm.* Thus the total amount of arsenic present was carried down.

The same is the case if water treated in this manner with one-thousandth millionth of its weight of arsenic is evaporated down to one-quarter its volume, and then treated with the ferric salt as above.

Thus one-thousandth of a m.grm. per litre of water is collected entirely by the ferric precipitate formed, and can be estimated exactly, rapidly, and correctly by Marsh's apparatus.

As a check, to 1 litre of distilled water we added 0.050 m.grm. of arsenic, then 5 c.c. of the ferric solution; boil, and filter after neutralisation with pure ammonia. The filtered liquor is treated as above with 20 grms. of nitric acid and 10 grms. of sulphuric acid; the excess of water and nitric acid is driven off by heat, and the remainder transferred to the Marsh apparatus. The amount of arsenic found is *nil*.

Thus, by this method we are enabled to detect and estimate exactly and without loss, a substance which is present to the extent of one part in one-thousand million parts of the material under examination.

I do not think that up to the present in experimental science or in any observations whatsoever, any other determination has been made with so great a degree of accuracy.

The same method may be applied with equal accuracy to waters highly charged with sea-salt (300 grms. per litre, pure or impure) of sulphate of potassium, nitre, chlorate of potassium, &c.

Consequently, we are enabled to estimate with precision the arsenic present in sea-water, in sea-salt, in mineral waters, the ordinary salts, acids, and bases, &c., with rapidity and perfect exactitude. It is only necessary to operate in neutral solution.

As for the application of this new method to the physiological or medico-legal detection of arsenic in the organs, we can first destroy the animal or vegetable matter by means of the nitrosulphuric mixture, and then take up the residue with boiling water; filter, cool, *partially* neutralise, and add the ferric solution so long as it does not show with ferrocyanide. The precipitate formed in the cold does not carry down the arsenic under these conditions. Filter again, add 5 c.c. of the ferric reagent, and bring the solution to boiling. After neutralisation with ammonia, filter, re-dissolve the ferric precipitate in a mixture of pure nitric and sulphuric acids, heat until all the nitrous fumes are given off and only nitric acid remains; dilute with water, and then pour direct into the Marsh apparatus. For complete success in the above case, this method requires a series of minute precautions which I shall make known in another paper.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

INTENSIFICATION OF CHEMICAL ACTION BY THE EMANATIONS FROM GOLD AND PLATINUM.*

By G. T. BEILBY.

WHEN a piece of gold or platinum foil is heated on a glass slip in an atmosphere containing the products of combustion of coal-gas a halo is formed on the glass surface surrounding the foil. This halo does not to any considerable extent consist of metallic particles, but is chiefly made up of the products of decomposition of the glass. If the halo is breathed on, the slight condensation of moisture on the surface dissolves the soluble salts, and sets free silica or an insoluble silicate in the form of thin films and spicules. When the water has evaporated a crystalline deposit is left on the surface.

By prolonged heating in the above atmosphere the whole of the exposed surface of the glass slip is slightly attacked, but the intensity of this attack is not to be compared with that which occurs in the near neighbourhood of the metal. The chemical action to which the formation of the halo is due, is therefore directly influenced by the presence of the hot metal.

It was at first thought that the metal foil might be acting simply by arresting radiant heat in its passage through the transparent glass, and thereby localising its effects; but this view is not supported by the subsequent experiments.

A number of experiments were made before it was sufficiently realised that a fairly free circulation of the atmosphere surrounding the metal is necessary if well marked halos are to be produced. It was also found that the partial exclusion of the products of combustion from the air-bath adversely affected the formation of halos.

When the glass slip with the metal foil is covered by another slip which is in contact with the metal, the halo is reduced to a sharp narrow outline of the foil.

If the cover slip is supported just out of contact with the metal, the halo is still a sharp outline, but now an image of the foil, less sharp, but also in outline, is formed on the

* Abstract of a Paper read before the British Association (Section A), Southport Meeting, 1903.

under surface of the cover slip. As the distance between the cover slip and the foil is increased, the halo widens and the image on the cover slip becomes a smooth patch without sharp outlines. These effects are obviously influenced by the more or less ample supply of the active constituents of the atmosphere which results from the greater or less freedom of circulation. This, in turn, is affected by the nearness of the cover slip to the metal.

A piece of platinum foil, 7 m.m. square, was used in a series of experiments in which the distances of the upper slip from the metal were 0.2 m.m., 1.5 m.m., 3 m.m., and 7 m.m.; an experiment was also made in which no cover slip was used. The temperature employed was about 500°, and the time of heating thirty minutes. At 0.2 m.m. distance halo and image* were both in outline. At 1.5 m.m. the halo was a band round the foil about 1 m.m. wide; the image showed no outline, but was in size and form similar to the foil. At 3 m.m. the halo had widened to over 2 m.m., part of this being got by encroaching on the area covered by the foil; the image was now circular, its diameter being equal to the diagonal of the square of the foil. At 7 m.m. the halo had widened to 3 to 4 m.m. on three sides, and to 8 m.m. on the fourth side; its general form was oval. The image was of the same form, and only a little smaller. It was evident in this case that the stream of emanations from the platinum had drifted across the slip under the influence of a current in the atmosphere of the air-bath. This evidence of drifting of the stream of emanations at once disposes of the idea that the formation of the halo and image is due in any way to the radiation or reflection of heat by the metal foil. The forms and dimensions of the halos and images strongly suggest that the emanations from the platinum are thrown upwards like a fountain, which spreads and descends on and around the foil. When the cover slip is at the maximum distance it is struck by the apex of the stream, and a large but faintly defined image is produced. When the distance of the cover slip is small, the stream is intercepted before it has spread much, and the halo and image are small and well-defined.

The decomposition of glass in the neighbourhood of hot metals appears to be a case of accelerated or intensified chemical action induced by the energy of the particles shot out from the hot metal. It occurred to me that some of the cases of catalytic action by platinum and other substances might be accounted for by the existence of active emanations surrounding the catalyte, and not merely by the actual contact of the molecules of the reagents with its surface. Experiments are now in progress to test this question.

ACTION OF MALT DIASTASE ON POTATO-STARCH PASTE.†

By ARTHUR R. LING.

Brown and Millar have shown that the so-called stable dextrin—one of the products of the hydrolysis of potato-starch paste by diastase—is converted by the further action of diastase into a mixture of about equal parts of *d*-glucose and maltose. The observation of Davis and Ling (see next abstract) that no *d*-glucose is formed when unrestricted diastase acts on starch paste, stands in apparent antithesis to this. However, the author has confirmed the result of Brown and Millar, and has found further that other isolated products of diastatic action yield a proportion of *d*-glucose when submitted to the further action of unrestricted diastase; thus the maltodextrin, α of Ling and Baker, when treated in 3 per cent solution with an active pre-

paration of diastase at 55° for 140 hours, gave the constants $[\alpha]_{D 3.93} 127.6^\circ$, $R_{3.93} 105.6$, corresponding approximately with maltose 90 per cent, *d*-glucose 10 per cent. The presence of 10.5 per cent of *d*-glucose in the product was proved by weighing the phenylglucosazone formed under standard conditions. Taking into account the fact that potato-starch paste is never completely converted into maltose, although the final product has the constants of that sugar, and that a substance is always present which is identical with the isomaltose of C. J. Lintner, the simple dextrin of Ling and Baker, and the dextrinose of Syniewski, which, when isolated and submitted to the action of diastase, yields *d*-glucose, the author suggests that the reason no *d*-glucose can be detected among the products of the action of unrestricted diastase on starch paste is that that sugar is immediately condensed by the action of the enzyme forming dextrinose. When, however, diastase is pre-heated, its condensing action is weakened, and the *d*-glucose formed can be isolated. Attempts to condense *d*-glucose or mixtures of it with maltose have not been successful.

ACTION OF MALT DIASTASE ON POTATO-STARCH PASTE.*

By BERNARD F. DAVIS, B.Sc., and ARTHUR R. LING.

In a previous paper (*Journ. Fed. Inst. Brew.*, 1902, viii., 475) it was shown that when malt diastase is heated in aqueous solution above the temperature at which the activity of the enzyme is at its optimum, namely 55°, the reaction with potato-starch paste at about 55° is not only slower, but different products are formed; thus *d*-glucose can be readily isolated from them after the reaction has been allowed to proceed for several hours. Special experiments, employing the same quantities of diastase which has not been heated in solution above 55°, show that *d*-glucose is not formed either from starch paste or from maltose. It therefore appears that the production of this sugar is connected with the pre-heating of the hydrolytic agent in solution above 55°. As a result of a very large number of new experiments, which will be published soon, the authors have arrived at the following conclusions:—

The effect of heating a solution of diastase as above indicated is to weaken its action and also to produce an alteration in the enzyme molecule, which is moreover a permanent one, for the diastase retains its altered properties when re-precipitated from its solution by alcohol and allowed to act on starch paste at or below 55°. The alteration of the diastase is assumed by the production of *d*-glucose when it acts on starch paste, and it appears to commence when a solution of the enzyme is heated below 60°; although, judging from the small amount of *d*-glucose formed by its action, the change at the last-named temperature is not complete. As the temperature of pre-heating the solution is increased, the amount of *d*-glucose it is capable of producing also increases, the maximum amount being obtained by the action of diastase which has been pre-heated in solution at 68° to 70° for fifteen to thirty minutes. Above this temperature the destruction of the enzyme is so rapid that a much larger proportion of it has to be employed to attain the stage of the reaction at which *d*-glucose appears. Still *d*-glucose is formed by diastase which has been restricted at temperatures up to 78°, and probably above this. It has been observed in all cases that, when after the maximum amount of *d*-glucose has been formed, the solution is kept at the temperature of hydrolysis, usually 55°, the sugar just mentioned diminishes in amount, and the occurrence of this apparent condensing action of the enzyme may probably explain the failure in several cases to detect *d*-glucose among the products of

* Throughout this paper the term "halo" is applied to the effect produced on the lower slip on which the metal lay, and "image" to that on the under surface of the cover slip.

† A Paper read before the British Association (Section B), Southport Meeting, 1903.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

hydrolysis (compare the preceding paper). The maximum amount of *d*-glucose formed in any case does not exceed about 12 per cent of the total hydrolytic products.

THE CHEMICAL AND PHYSICAL CHARACTERS OF THE SO-CALLED "MAD-STONE."*

By Dr. H. C. WHITE.

It is a widespread current superstition in the Southern States of America that the sting of a *venomous* snake and the bite of a *rabid* animal (dog, &c.) may be *detected* and discriminated from an innocuous wound, and the venom of the wound *extracted* by application of what is called the "mad-stone." Several of these stones came opportunely into the hands of the author, and an examination of their character was made.

The "mad-stone" of current superstition is a very rare concretionary calculus found in the gullet of the male deer. As extracted it resembles a water-worn pebble, oblong in form, varying in size, but not greater, perhaps, than 3 inches in length by 1½ inch in thickness. A smooth flat surface is given to one side by rasping. The examination was directed to the following points:—

1. *Chemical Composition*.—Found to be chiefly tri-calcic phosphate. Exact figures of analyses given.

2. *Adherence to Cut and Torn Flesh-wounds*.—Found to vary with the mechanical character of the wound and the mode of application of the stone, without regard to venomous or non-venomous character of the wound.

3. *Absorbing Power*.—Immersed in water the stones were found to absorb to an extent of 5 per cent of their weight. Applied to fresh wounds and carefully adjusted, blood and other fluid absorbed to a maximum extent of 2·3 per cent the weight of the stone.

4. *Character of Matter Absorbed*.—The stone after application to the wound is boiled with water, or *milk* (in accordance with the superstition). The fluid is discoloured, and is shown to be *toxic* in the case of a known venomous wound. No difference in discolouration observable in venomous and non-venomous wounds. That the stones are not *curative* is shown by the death of animals from venomous wounds after application of the stone.

The literature of the subject has been examined. The "mad-stone" superstition seems quite ancient. It was current in New England in Puritan times. The author has in his possession an authenticated "mad-stone" dating from 1654. This, however, is a moderately porous *sandstone*, entirely different from the modern "mad-stone" of the Southern States. It is peculiar in form, and appears somewhat as a water-worn pebble.

Specimens of the current "mad-stone" were exhibited in illustration of the paper.

Formation of Lactic Acid by the Action of Caustic Potash on the Pentoses.—K. Katsuyama.—Araki has shown that arabinose heated with soda-lye gives rise to the formation of formic and lactic acids. As xylose has quite a different constitution formula to arabinose, and as the recent researches of Salkowski show that the putrid fermentation of this sugar gives C_2H_5OH in considerable proportions, and as that of xylose does not give a trace of this alcohol, it appeared of interest to examine the action of KOH on xylose. The research described in this paper establishes the fact that this sugar is transformed, under these conditions, into lactic acid of fermentation. The same experiments made with arabinose confirm the results published by Araki; that is to say, they lead also to the formation of lactic acid of fermentation starting with arabinose.—*Berichte*, vol. xxxv., p. 669.

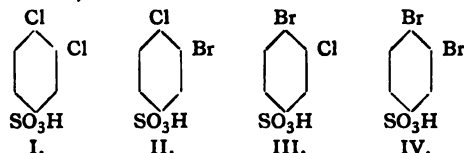
* A Paper read before the British Association (Section B), Southport Meeting, 1903.

ISOMORPHOUS SULPHONIC DERIVATIVES OF BENZENE.*

THE object the Committee have primarily in view is the crystallographic study of the complete series of sulphochlorides and sulphobromides derived from the isomeric dichloro-, dibromo-, and chlorobromo-benzenes.

The results obtained in the case of the para- and two of the three series of meta-derivatives have been referred to in previous reports. It may be pointed out that whereas no evidence was obtained that the 1:4-derivatives exist in polymorphic forms, the five compounds measured being strictly isomorphous,† in the case of the meta-derivatives, the 1:3:4-series formed an isotrimorphic group, the 1:3:5-series an isotetramorphous group.

During the past year Mr. Harding has determined the constants of five of the eight members of the 1:2:4-ortho-series, viz., the chlorides derived from the acids Nos. I., II., and IV., and the bromide of acid No. II. :—



Of the chlorides, I. and II. are practically identical crystallographically; the chloride of IV. was obtained in quite a distinct form, belonging, however, to the same crystallographic system. The bromide of II. was obtained in both these forms, so that it establishes a connecting-link between the two isomorphous series which evidently exist.

Great difficulty was experienced in making the measurements, owing to the low melting-points of the sulphohalides and the extraordinary way in which they crystallise (from a mixture of benzene and petroleum) in very thin micaceous plates; it was discovered, however, that by using petroleum of higher boiling-point more massive crystals could be obtained; forms fit for measurement were eventually secured by this artifice.

It would seem that the character of the solvent has a definite influence on crystalline form, especially in the case of substances which manifest polymorphism. When opportunity offers it will undoubtedly be desirable to study this question experimentally.

The anilides, which have higher melting-points than the halides, crystallise with much greater facility; the opportunity has been taken to study several of these. Mr. Harding finds that the orthodichloranilide exists in two forms—one orthorhombic, the other monosymmetric; and that whilst the dibromo- and bromochloro-anilides crystallise in a form isomorphous with the monosymmetric form of the dichloro-anilide, the fourth anilide crystallises in a second monosymmetric form.

Mr. Harding has also measured the 1:3-dibromo-2-sulphochloride, and has thus made a beginning with the 1:2:3-meta-series.

Although the material is available, it has been impossible hitherto to obtain two of the para-compounds and three 1:2:4-derivatives in forms suitable for measurement; it is hoped that the difficulty will be overcome, and that the experience which has been gained will make it possible to extend the investigation to the remaining terms of the meta- and ortho-series at no distant date. It is very desirable, for this purpose, to have large quantities of material at disposal, and that special apparatus should be devised which will make it possible to effect the crystallisation under constant conditions.

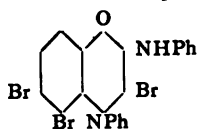
* Fourth Report of the Committee, consisting of Prof. H. A. Miers (Chairman), Dr. H. E. Armstrong (Secretary), Prof. W. P. Wynne, and Prof. W. J. Pope. (Drawn up by the Secretary). Read before the British Association (Section B), Southport Meeting, 1903.

† Mr. Harding has recently been able to obtain a sixth member of this series—the 1Cl:4Br:3sulphobromide—in measurable form, and finds that it is isomorphous with five which Mr. Gidden measured. Mr. Gidden did not succeed in preparing this compound.

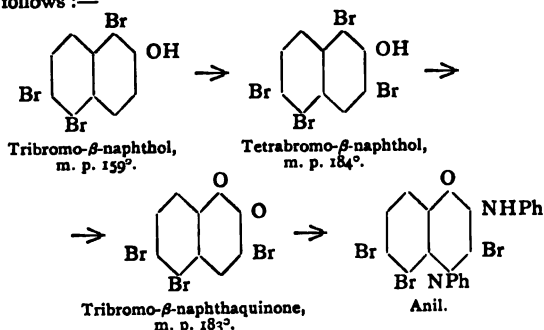
ISOMERIC NAPHTHALENE DERIVATIVES.*

DURING the past year proof has been obtained of the structure of the series of higher brominated derivatives prepared from 1:5:6-tribromo- β -naphthol which were referred to in last year's report; these compounds were then represented by formulæ containing a bromine atom in position 3 marked with a query. The following facts show that a correct view was then taken as to the position of this bromine atom.

The tetrabromo- β -naphthol (m. p. 184°), from which the higher brominated compounds are derived, is convertible by nitric acid into a tribromo- β -naphthaquinone (m. p. 183°), which aniline converts into the compound—



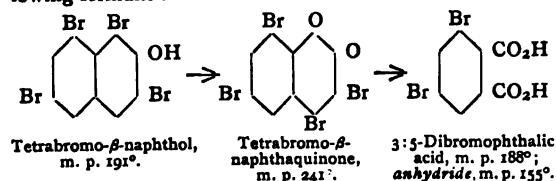
Such a substance can obviously only be formed from a quinone containing a bromine atom in position 3, not from one containing bromine in the alternative position 4. The relationship of the several compounds is therefore as follows:—



The structure has also been determined of the tetrabromo- β -naphthol, No. 3 (m. p. 191°; acetate, m. p. 210°), described in the 1901 report, which differs from all the other highly brominated naphthols in that it fails to give a nitro-bromo-keto-compound, being converted by nitric acid at the ordinary temperature into a tetrabromo- β -naphthaquinone (m. p. 241°).

This tetrabromo- β -naphthaquinone is oxidised by dilute nitric acid to a new dibromophthalic acid, which, by exclusion, must be the hitherto unknown 3:5-dibromophthalic acid; the quinone is therefore 3:4:6:8-tetrabromo- β -naphthaquinone.

The parent naphthol, which is derived from 1:3:6-tribromo-, not from 1:5:6-tribromo- β -naphthol, must therefore contain the bromine atoms in positions 1:3:6:8, the series of compounds being related as shown by the following formulæ:—

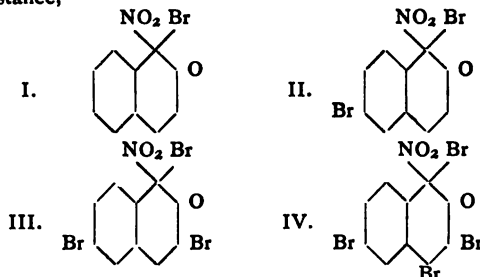


It follows from these results that, whilst the product of the further bromination of 1:3:6-tribromo- β -naphthol is 1:3:4:6-tetrabromo- β -naphthol, small quantities of the 1:3:6:8-tetrabromo-derivative are also formed.

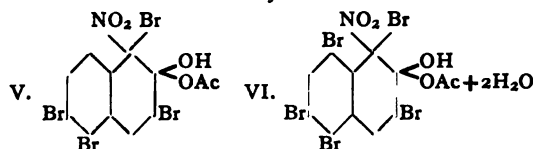
* Report of the Committee, consisting of Prof. W. A. Tilden (Chairman, and Dr. H. E. Armstrong (Secretary). (Drawn up by the Secretary). Read before the British Association (Section B), Southport Meeting, 1903.

The investigation of the bromo-naphthols has involved incidentally the study of the bromophthalic acids; the discovery of 3:4- and 3:5-dibromophthalic acids in the course of the work completes the series of dibromo-acids.

A systematic investigation of the nitro-bromo-keto-compounds formed by the action of nitric acid on the bromo- β -naphthols has led to the important discovery that whereas most of these substances are of normal composition—for instance,—

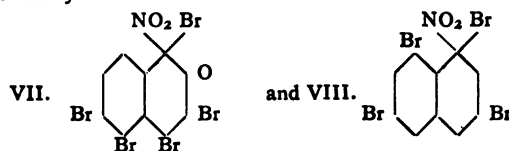


others can only be obtained in association either with acetic acid alone or with water of hydration. Thus—



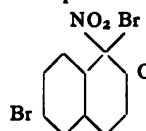
A similar addition of acetic acid takes place in the case of the keto-bromides (*infra*), but apparently not in the case of the keto-chlorides. These, however, as Zincke's researches show, in a few cases combine with alcohol.

Generally speaking, the nitro-bromo-keto-compounds increase in stability as the number of bromine atoms increases, so that, whilst the compound I., for instance, begins to decompose slightly above 0°, the compound II. is so stable that it may be left exposed during several months in the air at the ordinary temperature without undergoing change. But that structure and not merely the proportion of bromine present in the compound largely determines stability is shown by the fact that, for example, the compounds represented by the formulæ—

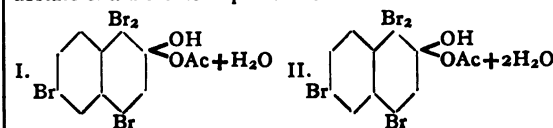


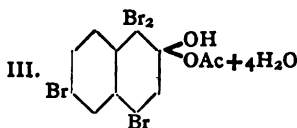
although rich in bromine, rapidly decompose at the ordinary temperature.

When bromine (one molecular proportion) is left in contact with the nitro-keto-compound—



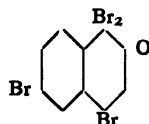
(derived from 1:6-dibromo- β -naphthol), suspended in glacial acetic acid and exposed to diffused light, nitrous fumes are slowly evolved and an arborescent mass of needles separates which appears to be the mono-hydrate (I.) of the acetate of a dibromo-naphthalene-keto-bromide—





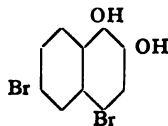
This substance melts at 63–65°; from the mother-liquors large slightly yellow prisms slowly separate which consist of the tetrahydrate III. The dihydrate II. is formed only under very special conditions, namely, when a solution of the nitro-bromo-keto-compound from 1-bromo- β -naphthol in acetic acid is acted on by bromine; it separates very slowly from solution in the form of small nearly colourless needles, melting at 81°.

If any one of these hydrated acetates be gently warmed with benzene a turbid solution is obtained; if this be dried with the aid of calcium chloride and slowly evaporated, it deposits magnificent nearly colourless plates of the simple keto-bromide,—



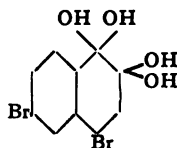
This substance apparently is the first representative of the class of naphthalene keto-bromides corresponding to the keto-chlorides which have been so fully studied by Zincke. When gently warmed, either alone or in the form of one of its hydrated acetates, with glacial acetic acid, it loses bromine and is converted into 4:6-dibromo- β -naphthaquinone (m. p. 171°); if the warming be continued the liberated bromine acts on this compound, converting it into 3:4:6-tribromo- β -naphthaquinone (m. p. 190°). Care is necessary, however, as otherwise the action may go further; a pentabromo-dinaphthyl-diquinone, $C_{20}H_3Br_5O_4$, then separates as a yellow crystalline insoluble powder. This compound is formed according to the equation $2C_{10}H_3Br_3O_2 = HBr + C_{20}H_3Br_5O_4$. A similar case of condensation was mentioned in last year's report.

Unlike the keto-chlorides, the keto-bromides do not give substituted naphthols when reduced either with stannous chloride and chlorhydric acid or with iodhydric acid (density 1.9); the sole product is 4:6-dibromo-1:2-dihydroxy-naphthalene,—



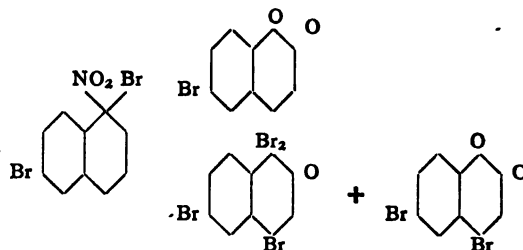
which is also obtained by reducing 4:6-dibromo-1:2-naphthaquinone. The corresponding diacetate, $C_{10}H_4Br_2(OAc)_2$, crystallises in large prisms melting at 157°.

The keto-bromide is probably first transformed into—



The discovery of 4:6-dibromo-2-keto-naphthalene-1-dibromide makes it possible to explain the production of 4:6-dibromo-1:2-naphthaquinone during the decomposition by heat of the nitro-keto-compound of 1:6-dibromo- β -naphthol. That the dibromo-quinone could not be formed by a mere bromination of 6-monobromo- β -naphthaquinone initially produced is shown by the fact that this bromination cannot be realised in practice. The real explanation is that the bromine initially split off from the nitro-keto-compound brominates the undecomposed re-

mainder of this substance, first displacing NO_2 ; a subsequent decomposition produces the 4:6-dibromo-quinone.



Now that the investigation has reached a stage when it is possible to give a complete account of the complex series of processes underlying the formation of the brominated naphthols, it is proposed to submit a considered discussion of the results for publication.

ON THE REDUCTION OF NITRATES BY SEWAGE.*

By Prof. LETTS, D.Sc., Ph.D., R. F. BLAKE, F.C.S., F.I.C.,
and
J. S. TOTTON, B.A.

THE object of this investigation was to ascertain to what extent, and with what rapidity, the nitrogenous constituents of sewage can be broken down by a suitably arranged scheme of purification, so that their nitrogen is evolved in the gaseous state. It is well known that in the most efficient systems of sewage purification by natural methods the resulting effluent is comparatively free from ammonia and organic nitrogen, but is charged with nitrates. These latter, however, do not correspond in amount with the quantities of the two former originally present, but are always less, and one of the authors, in conjunction with another chemist, has shown that during the treatment of sewage by the so-called "contact" or "bacteria" beds a considerable quantity of the combined nitrogen escapes as free nitrogen ("On the Chemical and Biological Changes Occurring during the Treatment of Sewage by the so-called Bacteria Beds," by Prof. Letts, D.Sc., Ph.D., and R. F. Blake, F.C.S., *B. A. Rep.*, 1901).

The researches of Gayon and Dupetit, Tacke, Adeney, and others have shown that nitrates are themselves decomposed when in contact with sewage with evolution of nitrogen or its oxides, and carbonic anhydride.

It therefore seemed possible that by a judicious combination of the two processes, i.e., production and destruction of nitrates, a considerable proportion and possibly most of the combined nitrogen present in sewage might be converted into free nitrogen, and as a consequence the resulting effluent be deprived of its fertilising properties in relation to vegetation.

Such a result might appear useless, and even wasteful, under ordinary circumstances, but in the case of the sewage of Belfast, and probably in that of other towns similarly situated, it is really necessary. At Belfast, at all events, one of the authors has shown that the growth in enormous quantities of the green sea-weed *Ulva latissima* and the resulting nuisance which occurs when it is washed ashore and putrefies—as happens each summer—is directly due to the fertilising properties of the sewage of the city, which is poured into the lough in an untreated condition.†

The experiments conducted by the authors consisted of:
(1) A study of the changes which occur when potassium

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

† This used to be the case, but works for the purification of the sewage are being pushed on rapidly, and at the present time a considerable proportion is being purified.

nitrate is added to the effluent from a septic tank, and the speed with which they occur; (2) an investigation as regards the cause of these changes; (3) the action of pure cultures of specific micro-organisms in broth containing potassium nitrate.

1. *The Chemical Changes Occurring when Potassium Nitrate is added to the Effluent from a Septic Tank.*

The method of experiment consisted in completely filling two similar bottles (which were then tightly stoppered), one with the septic-tank effluent alone and the other with the same effluent plus an accurately measured volume of a strong standard solution of potassium nitrate (1 c.c. = 10 m.gs. nitric nitrogen). Allowing the two bottles so filled to remain at the temperature of the laboratory for a given interval of time, and then examining their contents quantitatively as regards (a) dissolved gases, (b) nitrates, (c) nitrites, (d) free and albumenoid ammonia.

Practically all the experiments (which were eight in number) were made with mixtures of potassium nitrate and septic-tank effluent containing 2.5 parts of nitric nitrogen per 100,000 in the case of the nitrated samples. The chief general conclusions arrived at were as follow:—

(1) Potassium nitrate (and no doubt any other nitrate likely to be produced in a sewage effluent) is decomposed by the septic-tank effluent, and the nitric nitrogen is evolved, sometimes entirely as free nitrogen, sometimes partly as nitric oxide. Nitrous oxide may also be formed, but the evidence on that point is not as yet conclusive. (Gayon and Dupetit found all three gases). The action seems to vary with different samples of septic-tank effluent, but in four of the eight experiments the theoretical quantity of nitrogen [corresponding with the added nitrate] was found either as free nitrogen alone or along with nitric oxide.

There is no evidence from the authors' experiments to show that any considerable quantity of these gases are produced from either the free ammonia or the organic nitrogen present in the septic-tank effluent.

(2) The general character of the change is that of a combustion, the oxygen of the nitrate eventually appearing either partly or entirely in the form of carbonic anhydride.

(3) In some of the experiments a little nitrite was produced, but in the majority none was found at their conclusion.

(4) The destruction of the nitrate occurs with remarkable rapidity, and in most of the experiments the whole of the added nitrate—equivalent to 2.5 parts of nitric nitrogen per 100,000 of mixture—was decomposed in twenty-four hours.

(5) In addition to the decomposition of the nitrate and evolution of carbonic anhydride the fermenting liquid experiences other changes.

There is always a loss of free ammonia, and as a rule a gain in albumenoid ammonia, but the former generally exceeds the latter. Thus in six experiments the average loss of free ammonia amounted to 0.266 part per 100,000, while the corresponding gain in albumenoid ammonia was only 0.166, or rather less than half the preceding figure.

It may also be mentioned that in two of the experiments marsh gas was found, not only in the septic-tank effluent, but also in the nitrated fluid, and it is somewhat remarkable that more of the gas was found in the latter than in the former.

Towards the end of the investigation the effects of aëration were studied. Parallel experiments were made, in one of which the septic-tank effluent was thoroughly aërated before mixing it with the nitrate, while in the other the same quantity of nitrate was added to the non-aërated effluent. In both experiments the whole of the nitrate was decomposed in twenty-four hours with evolution of the equivalent quantity of nitrogen gas. In the aërated sample no marsh gas was formed, but a considerable excess of carbonic anhydride was produced, the total volume per litre of fluid being 57.1 c.c., whereas the amount corresponding with the added nitrate plus the oxygen dissolved from the air was $49.8 + 5.53 = 55.33$. In the non-aërated sample some marsh gas was formed, but considerably less carbonic anhydride.

The results obtained in this investigation suggest in part, at all events, an explanation of the production of free nitrogen in the "contact" beds commonly employed in the purification of sewage. These during the period they are in contact with air no doubt become charged with nitrates, and the latter are then destroyed when the beds are filled with sewage.

2. *Cause of the Decomposition of Nitrates when in Contact with a Putrefying Liquid.*

In order to ascertain whether the action was brought about entirely by the vital processes of micro-organisms, and was not due to enzymes excreted by them or to purely chemical changes, an apparatus was devised in which the septic-tank effluent was passed through a Chamberland filter and thence into a sterilised flask, from which it was drawn by a vacuum pump into two sterilised tubes of sufficient capacity, one of which contained a measured volume of the nitrate solution, and these tubes when filled were closed by pinch-cocks applied to indiarubber junctions. At the end of sixty-six hours analyses were made of the dissolved gases contained in the contents of both tubes, when it was found that they were practically identical, and that the nitrate had not been decomposed. The results of this experiment appear to be conclusive. The septic-tank effluent deprived of the micro-organisms which it contains has no action upon a nitrate. The decomposition of the latter must therefore be caused entirely by the vital processes of certain micro-organisms, and not by enzymic or chemical action.

3. *The Micro-organisms which Reduce Nitrates with Evolution of Nitrogen Gas or Oxides of Nitrogen.*

Gayon, Springer, Deherain, Maquenne, and others have isolated organisms from putrefying liquids which decompose nitrates with evolution of nitrogen or its oxides, but so far as can be judged from the printed abstracts of their work the identification of the species with known forms was either wanting or was incomplete. It occurred to the author that as the action is one of reduction it would be worth while to study the effects of those micro-organisms which are known to cause the evolution of hydrogen, such as *B. Amylobacter*, *B. Butyricus* (Botkin), *B. Lactis aërogenes*, and *B. Coli communis*, and as pure cultures or the latter happened to be available experiments were made with them.

An apparatus was constructed which permitted the introduction of pure cultures into a vessel filled with sterilised broth containing potassium nitrate from which the dissolved gases had been removed by boiling out in a vacuum.

With this apparatus experiments were first made on the action of pure cultures of *B. Coli communis* and *B. Lactis aërogenes* on broth alone. These were conducted at ordinary temperatures, and the fluid examined for dissolved gases as soon as a few bubbles of liberated gas had made their appearance. The dissolved gases were found (after removing carbonic anhydride) to consist entirely of hydrogen.

Experiments were then made with cultures of the same organisms and nitrated broth, and although they are not as yet completed the results so far obtained show that *B. Coli communis* liberates nitrogen from a nitrate in broth culture; *B. Lactis aërogenes* does not do so.

The authors desire to express their thanks to Professor Lorrain Smith, who supplied the pure cultures, and gave most valuable assistance and advice during the bacteriological part of the investigation.

Forthcoming Books.—*The Electrician* Printing and Publishing Company, Ltd., announce the early publication of the following:—Second Volume of Dr. J. A. Fleming's "Handbook of the Electrical Laboratory and Testing Room," 650 pages, fully illustrated, 14s. net. 1903 Revision of the "International Telegraph Convention and Telegraph and Telephone Service Regulations," 6s. net. New Edition of "Localisation of Faults in Electric Light Mains," by Mr. F. C. Raphael, 7s. 6d. net.

ON A METHOD FOR THE SEPARATION OF
COBALT FROM NICKEL AND THE VOLUMETRIC
DETERMINATION OF COBALT.*

By R. L. TAYLOR, F.I.C.

It has been long known that cobalt is precipitated from its solution as a higher oxide by the carbonates of barium, strontium, and calcium, in presence of chlorine or bromine. Long ago Rose proposed this as a means of separating cobalt from nickel, but he made the mistake of using a strongly acid solution. Of course the excess of acid was neutralised by the added carbonate, but the carbon dioxide thus produced retards enormously, if it does not altogether prevent, the complete precipitation of the cobalt. The author has found (*Memoirs of the Manchester Lit. and Phil. Soc.*, 1902, vol. xlvii., No. 11; and 1903, vol. xlvii., No. 12) that if a perfectly neutral and not too concentrated solution is used, cobalt is precipitated quantitatively as a black oxide in five or ten minutes by either barium or calcium carbonate in presence of bromine water. The two carbonates appear to act equally well, but the former is to be preferred if the subsequent removal of the added metal is desired. Whichever carbonate is used it should be in the precipitated form, and it is best made into a paste with water. If the liquid from which the cobalt is to be precipitated is acid, the acid may be neutralised by adding excess of the carbonate, but the liquid must then be well boiled to expel all the carbon dioxide, and then cooled before the bromine water is added. Not only does free carbonic acid prevent the precipitation of the cobalt, but zinc also considerably interferes with the reaction. A very small amount of that metal seriously retards the precipitation of the cobalt, and a large amount almost stops it altogether.

The author has ascertained the composition of the precipitated black oxide of cobalt by dissolving it in a mixture of hydrochloric acid and potassium iodide, and determining the amount of iodine liberated. It is fairly constant in composition, and approximates closely to the formulæ Co_9O_{14} and Co_7O_{11} . Which of these most correctly represents it composition he is unable to decide, but he suggests that its composition is sufficiently uniform to enable it to be used as a means for the volumetric determination of cobalt, by finding the amount of iodine which it liberates. The process has been tested by Mr. J. H. Davidson, B.Sc., in the assay of cobalt ores, and he finds it far more rapid than the processes generally in use, and at the same time quite sufficiently accurate for assay purposes.

NOTICES OF BOOKS

Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes. By C. R. ALDER WRIGHT, D.Sc. (Lond.), B.Sc. (Vict.), F.R.S. Second Edition. Edited and Partly Re-written by C. AINSWORTH MITCHELL, B.A. (Oxon.), F.I.C. London: Charles Griffin and Co., Ltd. 1903.

THE second edition of this book has been revised and partly re-written for the purpose of making it suitable for use as an analytical text-book. Hence the addition of a great deal of matter describing methods of analysis and the detection and determination of adulterants, which considerably increases the value of the book and enlarges its scope. As in the original edition, the manufacture of candles, soaps, and other products receives a large amount of attention, and a very useful chapter is given on the analysis of soap. These chapters have all been brought well up to date, and considerably enlarged. The subjects

dealt with in the volume include the general composition, nature, and sources of oils, butters, fats, and waxes, the physical and chemical properties of these substances, and the processes used for extracting, refining, and bleaching them. The data relating to the systematic description and classification of the oils appear to be most conveniently arranged for reference, and also to be very complete, considering the magnitude of the subject and the vast amount of literature dealing with it which has appeared in recent times.

Chemistry, Inorganic and Organic, with Experiments. By CHARLES LOUDON BLOXAM. Ninth Edition. Re-written and Revised by JOHN MILLAR THOMSON, LL.D., F.R.S., and ARTHUR G. BLOXAM, F.I.C. London: J. and A. Churchill. 1903.

SOME changes of importance have been made in the preparation of this edition of Bloxam's "Chemistry," notably among the illustrations, some of which are new, while many which appeared in earlier editions have been removed, and the arrangement also has been slightly altered. The general features of the book, however, remain the same, the method being strictly descriptive, though the constant reference to experiment makes it specially convenient for the use of the teacher in the preparation of lessons and lectures. As a work of reference it will still retain its place, especially where inorganic chemistry is concerned; the treatment of inorganic chemistry and organic in one volume has necessitated the condensation of the latter branch to an extent which seriously impairs its usefulness as a book to be put into the hands of the student. For conciseness sake many structural formulæ have been omitted in the belief that the reader may be trusted with the construction of them himself, but in all probability a large number of average students would rest content with endeavouring to commit to memory the formulæ as given, shirking the trouble necessary for the building up of the structural formulæ, and thus failing to get the best possible grasp of the principles involved. This condensation also has led to some omissions; for example, the important synthetic method known as Perkin's reaction for the preparation of cinnamic acid is by no means given the attention it deserves, and is not even mentioned by its familiar name, and in dealing with Reimer's reaction the question of the separation of the ortho- and para-compounds is not even touched upon. The sections on some of the useful applications of the principles of organic chemistry are, however, particularly full and good for a work of this nature.

CORRESPONDENCE.

PATENTS IN HOLLAND.

To the Editor of the Chemical News.

SIR,—Holland has long been almost the only highly civilised country in the world which does not grant patents of invention. We have received information, however, from our agents that the Dutch Government are now preparing a Patent Law, and its early presentation to Parliament was mentioned in the Queen's Speech. Holland is a member of the Union for the Protection of Industrial Property, consisting of nearly all the principal countries of the world, except Austria, Hungary, Russia, Persia, China, and Turkey, and each country in the Union has pledged itself to a large extent of reciprocity in connection with patents and trade marks.—We are, &c.,

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6, Lord Street, Liverpool,
September 23, 1903.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 8, August 24, 1903.

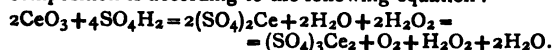
Piles consisting of Different Liquids with Identical Metallic Electrodes.—M. Berthelot.—The author has already shown that certain relations exist between the electromotive forces of the elements of piles with different metallic electrodes. He proceeds further with this research, and performs experiments on the elements of piles with different liquids, but terminated by identical electrodes. He then compares the observed results with those of theory. When the electrodes are identical, in principle there is no difference of potential in a cell composed of a single liquid, but only in elements composed of 2, 3, 4, 5, &c., separated liquids of different composition. He now examines only the elements in which there are two distinct and terminal liquids—that is to say, in contact with the metallic electrodes, which are identical. He operates with three metals—zinc, copper, and platinum. All the solutions possess equivalent concentrations—1 mol. = 5 litres for monovalent bodies; 1 mol. = 10 litres for divalent bodies.

Nos. 9 and 10.

These two numbers contain no chemical matter.

MISCELLANEOUS.

Peroxide of Cerium.—E. Baur.—By shaking up cerous sulphate in solution in carbonate of potassium liquor, in contact with air, we obtain an oxidation corresponding to the transformation of 83.6 per cent of cerium to the perceric state. In the presence of a body such as arsenite of soda (compare Manchot, *Zeit. Anorg. Chem.*, vol. xxvii., p. 420; *Bull. Soc. Chim.*, vol. xxviii., p. 406), this latter becomes oxidised, and the total quantity of fixed oxygen corresponds in a manner approaching the primary formation of the peroxide. The action of a cerous salt on a mixture of iodide of potassium and peroxide of hydrogen gives rise to the liberation of iodine, which is not opposed to the formation of a peroxide, but which, all the same, does not prove its existence. When we treat the salt described by Job (*Ann. de Chim.*, [7], vol. xx., p. 253) with sulphuric acid, oxygen is given off; apparently the decomposition is according to the following equation:—



The amount of active oxygen liberated, which theoretically should be double that remaining in solution in the form of H_2O_2 , is in reality greater, apparently on account of a partial and spontaneous decomposition of the peroxide of hydrogen.—*Zeit. Anorg. Chem.*, vol. xxx., p. 251.

Oxalo-niobic Acid.—Franz Russ.—The raw material used was columbite. The author first passes in review the different methods of treatment for the preparation of niobic acid. Oxalo-niobate of potassium is obtained by fusing together in a platinum crucible 16 grms. of fused niobic acid with 24.7 grms. of carbonate of potassium. After fusion, the mass is taken up with water, and the insoluble residue (about 0.185 gm. in weight) is separated; the solution is mixed with another solution containing 45.1 grms. of oxalic acid. The return is about 50 grms. The salt, which has the formula $\text{Nb}_2\text{O}_5 \cdot 3\text{K}_2\text{O} \cdot 0.6\text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, is crystalline, and occurs in spheroidal agglomerations. The sodium salt, which is more difficult to obtain, contains

$8\text{H}_2\text{O}$, the ammonium salt $3\text{H}_2\text{O}$, that of rubidium $4\text{H}_2\text{O}$. All the attempts made for the preparation of the alkaline salts of the type $2\text{Nb}(\text{C}_2\text{O}_4\text{K})_3 = \text{Nb}_2\text{O}_5 \cdot 5\text{K}_2\text{O} \cdot 10\text{C}_2\text{O}_3$ were failures. Solutions of niobic and of oxalic acids furnish crystals of which the composition varies considerably. Under certain experimental conditions, the author obtained by analysis figures comparable with those required by the formulæ $3\text{Nb}_2\text{O}_5 \cdot 2\text{C}_2\text{O}_3 \cdot 20\text{H}_2\text{O}$, $\text{Nb}_2\text{O}_5 \cdot \text{C}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Nb}_2\text{O}_5 \cdot \text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. In the presence of a small quantity of oxalic acid there is a tendency towards the formation of the body $\text{Nb}_2\text{O}_5 \cdot \text{C}_2\text{O}_3$; in the presence of an excess of this acid the tendency is to form $\text{Nb}(\text{C}_2\text{O}_4\text{H})_3$, from which we get the formation of the complex mixtures like $\text{Nb}_2\text{O}_5 \cdot 5\text{C}_2\text{O}_3 \cdot 21\text{H}_2\text{O}$. An aqueous solution of oxalo-niobate of potassium, $\text{Nb}_2\text{O}_5 \cdot 3\text{K}_2\text{O} \cdot 0.6\text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, at 2 per cent, precipitates the alkaline earthy salts and a large number of the metallic salts, but the salts of manganese, zinc, mercury (Hg'') are not precipitated. The decomposition of the binoxalate of barium by an excess of niobic acid, leads to the formation of the salt $\text{Nb}_2\text{O}_5 \cdot 5\text{BaO} \cdot 10\text{C}_2\text{O}_3 \cdot 20\text{H}_2\text{O}$. The action of dry chlorine gas transforms the oxalo-niobate of potassium into Nb_2O_5 and KCl , even at a temperature near to 100° . Tetra-chloride of carbon decomposes it in the same manner, but the reaction only commences at about 200° . With hydrochloric acid the decomposition takes place at a red heat. Sulphide of carbon gives sulphides at a temperature below red heat. The author has made some measurements of the conductivity of solutions of alkaline oxalo-niobates (K , Na , Am , Rb). The separation of tantalum and niobium by means of the complex oxalates cannot be effected.—*Zeit. Anorg. Chem.*, vol. xxxi., p. 42.

TO CORRESPONDENTS.

G. W. Thornhill.—The question is outside the scope of our paper. Apply to some medical journal.

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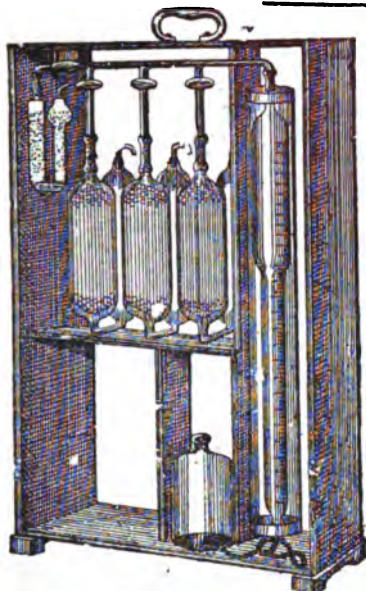
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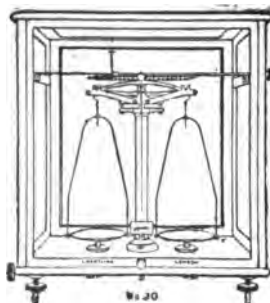
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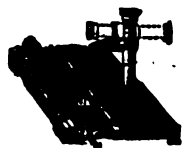
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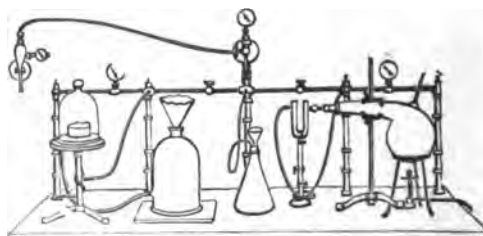
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2290.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 177).

CHAPTER III. (continued).

Proportion of β -Rays in the Radiation of Radium.

As I have already mentioned, the proportion of β -rays increases with increase of distance from the source of radiation. These rays never occur alone, and for great distances the presence of γ -rays is always discernible. The presence of very penetrating, undeflected rays in the radiation of radium was first observed by M. Villard. These rays constitute only a small portion of the radiation measured by the electrical method, and their presence escaped our notice in our first experiments, so that we believed falsely that the radiation at great distances contained only rays capable of deflection.

The following are the numerical results obtained with experiments made by the electrical method with an apparatus similar to that of Fig. 5. The radium was only separated from the condenser by the surrounding air. I shall indicate by the letter d the distance from the source of radiation to the condenser. The numbers of the second line represent the current subsisting when the magnetic field is acting, supposing the current obtained with no field equal to 100 for each distance. These numbers may be considered as giving the percentage of the total α - and γ -rays, the deflection of the α -rays having been scarcely observable with the conditions employed.

At great distances there are no α -rays, and the undeflected radiation is therefore of the γ kind only.

Experiments made at short distances:—

d , in centimetres	3.4	5.1	6.0	6.5
Percentage of undeflected rays	74	56	33	11

Experiments made at long distances with a product considerably more active than that which was used for the preceding series:—

d , in centimetres	14	30	53	80	98
Percentage of undeflected rays	12	14	17	14	16
d	124	157			
Percentage of undeflected rays	14	11			

It is thus evident that after a certain distance the proportion of undeflected rays in the radiation is approximately constant. These rays probably all belong to the γ species.

The following is another series of experiments in which the radium was enclosed in a very narrow glass tube, placed below the condenser and parallel to the plates. The rays emitted traversed a certain thickness of glass and air before entering the condenser:—

d , in centimetres ..	2.5	3.3	4.1	5.9	7.5	9.6	11.3
Percentage of rays not deflected ..	33	33	21	16	14	10	9
d			13.9	17.2			
Percentage rays not deflected ..			9	10			

As in the preceding experiments, the number of the second line approximate to a constant value, when the distance d increases, but the limit is reached for smaller distances than in the preceding series, because the α -rays

have been more completely absorbed by the glass than the β - and γ -rays.

The following experiment shows that a thin sheet of aluminium (0.01 m.m. thick) absorbs principally α -rays. The product being placed 5 c.m. from the condenser, the proportion of rays other than β , when the magnetic field is acting, is about 71 per cent. When the same substance is covered with the sheet of aluminium, the distance remaining the same, the radiation transmitted is found to be almost totally deflected by the magnetic field, the α -rays having been absorbed by the aluminium. The same result is obtained when paper is used as the absorbing screen.

The greatest part of the radiation of radium consists of α -rays, which are probably emitted principally by the superficial layer of the radiating matter. When the thickness of the layer of radiating matter is varied, the intensity of the current increases with this thickness; the increase is not proportional to the thickness for the whole of the radiation; it is, moreover, more considerable for the β -rays than for the α -rays, so that the proportion of β -rays increases with the thickness of the active layer. The source of radiation being placed at a distance of 5 c.m. from the condenser, it is found that for a thickness equal to 0.4 m.m. of the active layer, the total radiation is given by the number 28, and the proportion of the β -rays is 29 per cent. By making the layer 2 m.m. thick, i.e., five times as thick, a total radiation equal to 102, and a proportion of β -rays equal to 45 per cent are obtained. The total radiation which exists at this distance has therefore been increased in the ratio of 3.6, and the β -radiation has become five times as strong.

The preceding experiments were made by the electrical method. When the radiographic method is used, certain results seem to be in contradiction with what precedes. In the experiments of M. Villard, a beam of radium rays, subjected to the action of the magnetic field, was received on to a pile of photographic plates. The undeflected and penetrating γ -beam passed through all the plates, leaving its trace on each. The deflected β -beam produced an impression on the first plate only. This beam appeared therefore to contain no rays of great penetration.

On the contrary, in our experiments a beam which is propagated in the air contains at the greatest distances accessible to observation about 9/10 of β -rays, and the same is the case when the source of radiation is enclosed in a little sealed glass vessel. In M. Villard's experiments, these deflected and penetrating β -rays did not affect the photographic plates beyond the first, because they are to a great extent diffused in all directions by the first solid obstacle encountered, and no longer form a beam. In our experiments the rays given off by radium and transmitted through the glass of the vessel were also probably scattered by the glass, but the vessel being very small would itself act as a source of β -rays at its surface, and we were able to follow the course of the latter to a great distance from the vessel.

The cathode rays of Crookes tubes can only traverse very thin screens (aluminium screens of 0.01 m.m. thickness). A beam of rays striking the screen normally is scattered in all directions; but the diffusion becomes less with diminishing thickness of the screen, and for very thin screens the emerging beam is practically the prolongation of the incident beam.

The deflected β -rays of radium behave in a similar manner, but the transmitted beam experiences, for the same thickness of screen, a much slighter modification. According to the experiments of M. Becquerel, the very readily deflected β -rays of radium (those with a relatively small velocity) are powerfully scattered by an aluminium screen of thickness 0.1 m.m.; but the penetrating and less deflected rays (rays of the cathode kind of great velocity) pass through this screen without being sensibly diffused, whatever be the inclination of the screen to the direction of the beam. The β -rays of great velocity penetrate without diffusion a much greater thickness of paraffin (several centimetres), and in this the curvature of the beam produced by the magnetic field can be traced. The thicker the

* Thesis presented to the Faculté des Sciences de Paris.

screen, and the more absorbent the material of which it is composed, the greater is the modification of the deflected primitive beam, because, with increasing thickness of screen, diffusion occurs progressively among fresh groups of rays of increasing penetration.

The β -rays of radium experience a diffusion in passing through the air, which is very marked for readily deflected rays, but which is much slighter than that produced by equal thicknesses of solid substances. For this reason, the β -rays traverse long distances in the air.

Penetrating Power of the Radiation of Radio-active Bodies.

Since the beginning of the researches on radio-active bodies, investigations of the absorption produced by different screens upon the rays given off by these bodies have been carried on. In a previous paper on this subject I gave figures (quoted at the beginning of this work) representing the penetrating power of uranium and thorium rays. Mr. Rutherford has made a special study of the radiation of uranium, and proved it to be heterogeneous. Mr. Owens has arrived at the same results for thorium rays. When the discovery of strongly radio-active bodies immediately followed upon this, the penetrating power of their rays was also studied by various physicists (Becquerel, Meyer and von Schweidler, Curie, Rutherford). The first observations brought to light the complexity of the radiation, which seems to be a general phenomenon, and common to the radio-active bodies. In them we have sources which give rise to a variety of radiations, each of which has a power of penetration proper to itself.

Radio-active bodies emit rays which are propagated both in the air and *in vacuo*. The propagation is rectilinear; this fact is proved by the distinctness and shape of the shadows formed by interposing bodies opaque to the radiation between the source and the sensitive plate or fluorescent screen which serves as receiver, the source being of small magnitude in comparison with its distance from the receiver. Various experiments demonstrating the rectilinear propagation of uranium, radium, and polonium rays have been made by M. Becquerel.

It is interesting to know the distance that rays can travel in air. We have found that radium emits rays which can be detected in the air at a distance of several metres from the source. In certain of our electrical determinations, the action of the source upon the air of the condenser made itself felt at a distance of between 2 and 3 metres. We have also obtained fluorescent effects and radiographic impressions at similar distances. The experiments are not easily carried out, except with very intense radio-active sources, because, independently of the absorption by the air, the action upon a given receiver varies inversely as the square of the distance from a source of small dimensions. This radiation, which travels a long distance in the case of radium, comprises rays of the cathode kind and rays which are undeflected; however, the deflected rays predominate, according to the results of the experiments already mentioned. The greater part of the radiation (α -rays) is, on the contrary, limited in air to a distance of about 7 c.m. from the source.

I made several experiments with radium enclosed in a little glass vessel. The rays emerging from the vessel, after traversing a certain space of air, were received in a condenser, which served to measure their ionising capacity by the usual electrical method. The distance, d , from the source to the condenser was varied, and the current of saturation, i , obtained in the condenser was measured. The following are the results of one of the series of determinations. (See next column).

After a certain distance, the intensity of radiation varies inversely as the square of the distance from the condenser.

The radiation of polonium is only propagated in air to a distance of a few centimetres (4 to 6 c.m.) from the source of radiation.

In the case of the absorption of radiations by solid screens, we find another fundamental difference between

d , c.m.	i .	$(i \times d^2) \times 10^{-3}$.
10	127	13
20	38	15
30	17.4	16
40	10.5	17
50	6.9	17
60	4.7	17
70	3.8	19
100	1.65	17

radium and polonium. Radium emits rays capable of penetrating great thicknesses of solid matter, *e.g.*, several centimetres of lead or of glass. The rays which have passed through a great thickness of a solid body are extremely penetrating, and it is practically impossible to absorb them entirely by any material whatever. But these rays form only a small fraction of the total radiation, the greater part of which is absorbed by a slight thickness of solid matter.

Polonium emits rays which are readily absorbed, and which can only pass through extremely thin screens.

The following are figures showing the absorption produced by an aluminium lamina of thickness 0.01 m.m. This lamina was placed above and almost in contact with the substance. The direct radiation and that transmitted by the aluminium were measured by the electrical method (apparatus of Fig. 1); the current of saturation was practically obtained in every case. I have represented the activity of the radiating body by a , that of uranium being unity.

	a .	Fraction of radiation transmitted.
Chloride of barium and radium	57	0.32
Bromide " "	43	0.30
Chloride " "	1200	0.30
Sulphate " "	5000	0.29
" " "	10,000	0.32
Metallic bismuth and polonium	—	0.22
Compounds of uranium	..	0.20
Compounds of thorium in a thin layer		0.38

We see that radium compounds of different nature and activity give very similar results, as I have already pointed out in the case of uranium and thorium compounds at the beginning of this work. We see also that, taking into account the whole of the radiation, and with a given absorbent screen, the different radio-active bodies can be arranged in the following decreasing order of penetrating power:—Thorium, radium, polonium, uranium.

These results are similar to those which have been published by Mr. Rutherford.

Mr. Rutherford also finds that the order is the same when air is the absorbent substance. But it is probable that this order has no absolute value, and would not be maintained independently of the nature and thickness of the screen. Experiment shows, indeed, that the law of absorption is very different for polonium and radium, and that, for the latter, the absorption of the rays of each of the three groups must be considered separately.

(To be continued).

Action of Mixed Organo-magnesium Compounds on Bodies with a Nitrated Function.—Louis Meunier.

—The author has examined the action of some of these bodies, such as the ethereal solution of ethyl-iodide of magnesium, on ammonia, on aniline, and on diazoamidobenzene; and of ethyl-bromide of magnesium on phenylhydrazine. The above reactions enabled him to obtain the methanolic carbides from the iodides or bromides of the corresponding alcohols.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 8.

ESTIMATION OF ARSENIC IN SEA-WATER, SEA-SALT, ROCK-SALT, MINERAL WATERS, &c., AND IN SOME OF THE ORDINARY REAGENTS.

By ARMAND GAUTIER.

It has been known for some time that sea-water contains a small proportion of arsenic. I have shown that it is partly in solution and partly organic, contained in the constituents of *plankton*, especially in the microscopic algæ, in which it accompanies the iodine (*Comptes Rendus*, vol. cxxxv., p. 833); but, up to the present, the difficulty of collecting the whole of these traces of arsenic in the presence of a large quantity of chlorides and other salts has made any exact determination of this element in salt waters impossible.

The new method I have described recently (see *CHEMICAL NEWS*, vol. lxxxviii., p. 177) enables us, on the contrary, to estimate the arsenic in sea-water, sea-salt, and rock-salt with the greatest ease.

For the purpose of my research on physiological arsenic, I have been obliged to estimate it also in distilled water and in the reagents generally met with in legal medicine.

Sea-water, Salt Springs.—In the sea-water from the Atlantic (coast of Brittany) I attempted to estimate the arsenic in its three forms—*mineral, organic, and organised*.

The water, filtered through biscuit porcelain, was treated with 10 c.c. per litre of ferric sulphate free from arsenic (this ferric solution contained 30 grms. of Fe_2O_3 per litre), boiled, saturated with ammonia, and filtered. The mineral arsenic was estimated, as has been described (*loc. cit.*), by dissolving the ferric precipitate in dilute sulphuric acid, and transferring directly to the Marsh apparatus. For the organic arsenic, the solution from which the above ferric precipitate was obtained was treated, after filtration, with 70 c.c. of pure nitric acid, and distilled to dryness on a sand-bath in a glass retort fitted with a condenser terminating in a Will and Varrentrap tube containing a warm solution of pure potash, the whole being connected together with ground joints. It was ascertained that under these conditions the glass did not give up any perceptible amount of arsenic to the acid (less than 0.0003 m.grm.). The non-condensed acid fumes and the chloride passes bubble by bubble through the purified potash (this contained 0.0044 m.grm. of As per 100 c.c., and 0.0006 m.grm. for the amount used) destined to collect and destroy the fumes of chloride of arsenic which might be produced. After complete desiccation and gentle calcination of the dry residue in the retort, the acid liquor distilled and the alkaline solution in the tubes were mixed, neutralised, treated with 10 c.c. of ferric solution, and boiled, &c., as before.

After making all corrections for traces of arsenic introduced, the following results were obtained:—

A. Sea-water taken 30 Kilometres off the Coast of Brittany at 5 Metres below the Surface.

	M.grms. per litre of water.
Mineral arsenic	0.009
Organic	0.0008 (about)
Organised	Not weighable in 1 litre.

B. The same Sea-water.

Total arsenic 0.010

The following determinations are of interest, having been made on samples of water from the Atlantic from the neighbourhood of the Azores, in the same vertical line but at different depths. These samples were collected with all possible precautions by His Highness the Prince of Monaco, to whom I offer my sincere thanks:—

Water from the Atlantic (Azores).

	Depth. Metres.	Arsenic per litre. M.grms.
S. 1394	10	0.025
—	1335	0.016
S. 1427 ($t=2.7^\circ$)	5943 (6 or 8 metres from the bottom) ..	0.080

Thus it appears that, in the neighbourhood of volcanic regions, arsenic is abundant, especially at great depths. We shall see later on that arsenic comes principally from volcanic action.

The waters from salt springs are all more or less arsenical, especially ferruginous waters and those containing sodic chloride. This new method enables us to estimate the arsenic present with great precision. Chloride of sodium does not interfere at all with the carrying down of this metalloid by the ferric salt, which becomes insoluble when heated. As an example, I will give the estimation I made on the salt water from Misserey, near Besançon. This water, which was almost saturated with salt (it contained 326 grms. per litre) gave—

Arsenic per litre 0.010 m.grm.

This is the same amount that is contained in the water at the entrance to the English Channel at the surface.

Sea-salt, Rock-salt.—It appeared to me to be probable that sea-salt from sea-water rich in arsenic might contain a sensible proportion of this element. This was confirmed by the following analyses:—

Origin.	M.grms of arsenic per 100 grms. of salt.
Fine white salt—	
Coast of Brittany	0.003
Sands of Olonne	0.001
Grey kitchen salt—	
Sands of Olonne (Atlantic):—Soluble, 0.035; insoluble, 0.010	0.045
Salt said to be English*—	
Bought at Potin's, Paris	0.015
Rock salt—	
Stassfurth (beautiful, transparent)	0.0025
St. Nicholas. near Nancy:—Soluble, 0.009; insoluble, 0.005	0.014
Mountain of salt at Djebel-Amour (South Oran)	0.005
Chloride of sodium, fused at a red heat	0.030
Chloride of sodium, collected in a volcanic fissure on Vesuvius	0.175

* This salt was very fine and opaque, and appeared to be mixed with a small proportion of spices.

Thus, chloride of sodium always contains arsenic, especially if it is of direct volcanic origin, as shown by the last sample.

We get further information also from these analyses. Of all the common kinds of salt, the grey kitchen salt is the richest in arsenic. It constitutes one of the principal sources from which we draw our daily necessary supply of arsenic, which certain of our organs seize upon with such avidity.

From the medico-legal point of view, due regard must be given to the continuous introduction of arsenic by means of kitchen salt. But it must be remarked that the quantities absorbed by this means are minimal (about a decimilligram. per month). Above all, it must not be forgotten that I have proved that the liver, the blood, the stomach, the muscles, &c., of mammals do not contain arsenic in their normal states, or at most an amount lower than $\frac{1}{100}$ th of a milligram. per 100 grms. after deducting that due to the reagents, especially the sulphuretted hydrogen.

Various Reactions.—Finally, I wished to determine, by means of my new method, the amounts of arsenic that the

supposed pure reagents had introduced into the estimations made by my old method. The following results were obtained :—

	Arsenic per litre. M.grm.
Water, distilled in a tinned copper retort (treated with 1 grm. CO_3Na_2 per litre)	0'0007
Water, distilled in a glass retort with 1 per cent of pure CO_3NaH	0'0011
Pure commercial ammonia	Per 100 c.c. 0'0010
Ammonia made from sulphate of ammonia free from arsenic, and caustic soda reputed pure	0'0033
Pure commercial bicarbonate of soda	Per 100 grms. 0'016
Pure commercial nitre	0'0015
Reputed pure sulphate of potassium	0'006
The same, purified by $(\text{SO}_4)_3\text{Fe}_2$, containing 30 grms. Fe_2O_3 per litre	0'0000
Purified ferric sulphate	Per 30 grms. Fe_2O_3 . 0'0004
Specially purified nitric acid	Per 100 grms. 0'00023
Concentrated aqueous solution of sulphurous acid gas	Per 100 c.c. 0'005
Sulphuretted hydrogen, obtained from ordinary FeS and HCl , and washed carefully with acids and with water	A considerable quantity. 0'0008*
The same sulphuretted hydrogen, purified	In 30 grms. 0'0000
Pure zinc	0'0000

* The whole of this arsenic was carried by a current of bubbles of medium velocity during two hours through pure nitric acid at 80° , placed in a long-necked flask, not giving arsenic. In a future paper I will describe the method of purifying sulphuretted hydrogen.

It will be observed that most of the so-called pure reagents used habitually in the detection of arsenic by the old method, such as the distilled water, the nitric and sulphuric acids, the bisulphites, the ammonia and its carbonate, and especially the sulphuretted hydrogen, contain a trace—and this latter gas a considerable quantity—of arsenic. The amount introduced by my new method is nil, but the same is not the case when we have recourse to the old ones. It is quite possible, by using impure sulphuretted hydrogen, to obtain more than 0'001 grm. of arsenic.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

ON THE RESOLUTION OF ELEMENTARY SUBSTANCES INTO THEIR ULTIMATES, AND ON THE SPONTANEOUS MOLECULAR ACTIVITY OF RADIUM.*

By HENRY WILDE, D.Sc., F.R.S.

THE author refers to several of his papers published by the Society on the genesis of elementary substances, and on the multiple proportions of their atomic weights, wherein certain gaps appeared in the several series in his tables which have since been filled up by scandium, germanium, helium, argon, neon, krypton, and xenon. The remarkable properties of radium bring about further realisations of the predictions made in the author's earlier papers. The series H_2N has long been remarkable for the property of phosphorescence which some of its lower members possess above those of other series of elements. Radium has been shown by its discoverers, M. and Mme. Curie, to be the next higher member of the calcium, strontium, and barium series of alkaline earth metals, and that its halogen com-

pounds are permanently self-luminous. The author had previously indicated the remarkable interruption in the regularity of his multiple series H_2N through the absence of elements of atomic weights 160 and 184 respectively. As there is only one place vacant higher in this series for an analogue of calcium, strontium, and barium, radium is identified by the author as the tenth elementary condensation of H_2N , with an atomic weight of 184 and a specific gravity of 4'8, as shown in his tables. The author has shown in former papers that helium was the unknown typical molecule of the same series, with an atomic weight of 2, and had previously indicated the probability of the resolution of the higher members of each series into their elementary typical molecules. The production of helium from radium by Professors Rutherford, Soddy, and Ramsay confirms the author's prevision in the case of the series H_2N , and this result may lead to the resolution of the higher members of other series into their ultimates.

The discovery of MM. Curie and Laborde of the spontaneous molecular activity of radium also confirms the views expressed by the author in the course of his lecture delivered before the Society in 1902, with reference to the spontaneous molecular and molar activity of endothermic substances.

DUTY-FREE ALCOHOL FOR SCIENTIFIC RESEARCH.*

THE Committee appointed at the Glasgow meeting in 1901 were unable to report in 1902, as they were at the time of the Belfast meeting in the midst of their negotiations with the Board of Inland Revenue.

After a preliminary meeting and correspondence in the winter of 1901-2 the Committee received information that the Government were willing to adopt a clause in the Budget Bill of 1902 which would permit the use of duty-free alcohol under conditions to be laid down by the Board of Inland Revenue. When the Budget Bill was passed a deputation from the Committee waited on the Chairman of the Board, and after full discussion the Committee agree to confine their application at the present time to the use of duty-free alcohol (ethyl and methyl) and of alcoholic derivatives for the purposes of research work and higher teaching in the laboratories of universities, colleges, and public institutions.

At the request of the Chairman of the Board of Inland Revenue the Committee drew up the following statement :—

"To the Chairman of the Board of Inland Revenue.

"August 6, 1902.

"SIR,—At the meeting of the British Association held at Glasgow last year a Committee was appointed to approach the Inland Revenue Commissioners to urge the desirability of securing the use of pure alcohol duty-free for the purposes of scientific research.

"It was pointed out at the Glasgow meeting that the low price of pure alcohol and its derivatives on the Continent and the high duty payable in the United Kingdom, severely handicapped research workers here in chemistry, physiology, and pathology, and to a smaller extent in zoology and botany. In the recent debates on the Budget Bill this disadvantage was recognised, and steps were taken with a view to remedy the evil.

"In the United States, where alcohol is taxed, permits are granted to scientific institutions of certain rank enabling them to obtain duty-free alcohol for use in their laboratories. The conditions under which these permits are granted by the United States Treasury have been obtained by this

* Abstract of a Paper read before the Manchester Literary and Philosophical Society, October 6, 1903.

* Report of the Committee, consisting of Sir H. Roscoe (Chairman), Prof. H. B. Dixon (Secretary) Sir Michael Foster, Sir A. W. Rüchler, Dr. T. E. Thorpe, Prof. W. H. Perkin, and Prof. W. D. Halliburton. Read before the British Association (Section B), Southport Meeting, 1903.

Committee. A copy of these regulations was placed in your hands at the interview you were good enough to grant on the 9th inst to members of this Committee.

"In accordance with your request we have obtained some statistics as to the amount of alcohol (and its derivatives) used in English laboratories for higher teaching and research work. It has not been possible to obtain complete details, but the following figures, which are the average number of gallons used per annum during the last three years in the laboratories at Cambridge, at Owens College, and the Yorkshire College, may be taken as typical:—

	Absolute ethyl alcohol.	Recti- fied spirit.	Absolute methyl alcohol.	Ethyl ether.	Methyl- ated spirit.
I. Cambridge (<i>University and College Laboratories</i>).					
Chemical Laboratories..	30	30	—	60	500
Pathological " ..	15	—	—	10	
Physiological " ..	10	10	—	10	
Zoological and Botanical Laboratories " ..	20	—	—	—	
II. Owens College.					
Chemical Laboratories..	50	—	20	80	100
Pathological " ..	15	—	—	5	5
Physiological " ..	5	—	—	—	25
Zoological and Botanical Laboratories " ..	5	—	—	1	120
III. Yorkshire College.					
Chemical Laboratories..	15	—	12	25	50
Medical Department ..	—	—	—	—	150

It should be pointed out that if pure alcohol could be obtained duty-free more would be used in scientific work instead of the methylated spirit now used whenever possible.

"From the table given it will be seen that the chief demand in scientific laboratories is for pure ethyl alcohol and pure ethyl ether. But other alcohols (*e.g.*, methyl alcohol) and other derivatives of alcohols (*e.g.*, methyl and ethyl iodides) and ethereal salts (*e.g.*, malonic ether) are largely used in organic chemistry. These reagents are at present mainly imported from Germany, and pay duty to the Customs. There is therefore a desire that such ethereal compounds might be imported duty-free for scientific use.

"In the request that we now make for the use of duty-free ethyl alcohol and its derivatives, for the purpose of higher teaching and research, we would point out that the alcohol (or other reagent) is destroyed or contaminated beyond recovery by the use to which it is put, and such destruction or contamination could be certified by the director of the laboratory.

"In the opinion of the Committee there would be no difficulty in arranging for one distributing station in each university centre to supply the several laboratories of that centre."

On October 22 the Committee received from the Board a draft of the suggested regulations under which it was proposed to authorise the issue, in accordance with section 8 of the Finance Act, 1902, of pure spirit duty-free for purposes of scientific research and education. The Board asked for observations on the proposed regulations.

The Committee had copies of these proposed regulations sent to the directors of the chief laboratories in the country, with a request that they would forward any suggestions they might wish to make to the Committee. After considering the suggestions sent in, the Committee submitted their observations to the Board, who adopted the alterations suggested, and informed the Committee that methyl alcohol might be obtained under the same regulations.

The Committee, with the permission of the Board of Inland Revenue, published the regulations in the *Times* and other newspapers with the accompanying explanatory letter:—

"DUTY-FREE ALCOHOL FOR RESEARCH.

"To the Editor of the *Times*."

"December 15, 1902.

"SIR,—It has long been felt by scientific workers in this country that a serious drawback to the prosecution of research lies in the fact that the full and very heavy duty has to be paid on pure alcohol, as distinguished from methylated spirit, largely used in scientific laboratories where higher teaching and research are carried on. And this appeared to be a hardship in the first place because the alcohol thus used is either destroyed or rendered useless for potable purposes, and in the second place because no such duty is paid in Germany, France, or the United States, and thus the British is heavily handicapped as against the foreign worker.

"At the meeting of the British Association held last year in Glasgow, a Committee was appointed with instructions to approach the Board of Inland Revenue with the object of endeavouring to secure the removal of this grievance—a grievance which was recognised by Government in the Budget Bill of this year. We are now glad to report that the Board has met our suggestions in the fairest possible manner with an obvious desire to extend facilities for scientific research in the direction indicated, as a perusal of the regulations which we enclose will show.

"The Secretary to the Board of Inland Revenue informs us that pure 'methyl alcohol,' also much used in chemical research, may be obtained under the same regulations, and should smaller quantities of methyl alcohol be required than the minimum permitted in the case of ethyl alcohol, the Board will consider special applications to that effect. —We are, &c.,

"H. E. ROSCOE, Chairman.

"H. B. DIXON, Secretary to the Committee."

(Enclosure).

Regulations for the Use of Duty-free Spirit at Universities, Colleges, &c.

1. An application must be made by the governing body or their representatives, stating the situation of the particular university, college, or public institution for research or teaching, the number of the laboratories therein, the purpose or purposes to which the spirits are to be applied, the bulk quantity likely to be required in the course of a year, and, if it amounts to fifty gallons or upwards, the name or names of one or more sureties, or a guarantee society to join in a bond that the spirits will be used solely for the purpose requested and at the place specified.

2. The spirits received at any one institution must only be used in the laboratories of that institution, and must not be distributed for use in the laboratories of any other institution, or used for any other purpose than those authorised.

3. Only plain British spirits or unsweetened foreign spirits of not less than 50 degrees over-proof (*i.e.*, containing not less than 80 per cent by weight of absolute alcohol) may be received duty-free, and the differential duty must be paid on the foreign spirits.

4. The spirits must be received under bond either from a distillery or from an Excise or Customs general warehouse, and (except with special permission) in quantities of not less than nine bulk gallons at a time. They will be obtainable only on presentation of a requisition signed by the proper supervisor.

5. On the arrival of the spirits at the institution the proper revenue officer should be informed, and the vessels, casks, or packages containing them are not to be opened until he has taken an account of the spirits.

6. The stock of spirits in each institution must be kept under lock in a special compartment under the control of a professor or some responsible officer of the university, college, or institution.

7. The spirits received by the responsible officer of the

institution may be distributed by him undiluted to any of the laboratories on the same premises.

8. No distribution of spirits may be made from the receiving laboratory to other laboratories which are not within the same premises.

9. A stock-book must be provided and kept at the receiving laboratory, in which is to be entered on the debit side an account of the bulk and proof gallons of spirits received with the date of receipt, and on the credit side an account of the bulk and proof gallons distributed to the other laboratories. A stock-book must also be kept at each other laboratory, in which must be entered on the day of receipt an account of the bulk and proof gallons of spirits received from the receiving laboratory. These books must be open at all times to the inspection of the revenue officer, and he will be at liberty to make any extract from them which he may consider necessary.

10. The quantity of spirits in stock at any one time must not exceed half the estimated quantity required in a year where that quantity amounts to 20 gallons or upwards.

11. Any contravention of the regulations may involve the withdrawal of the Board's authority to use duty-free spirits.

12. It must be understood that the Board of Inland Revenue reserve to themselves full discretion to withhold permission for the use of duty-free spirit in any case in which the circumstances may not seem to them to be such as to warrant the grant of it.

NOTE.—"Proof spirit" is defined by law to be such as at the temperature of 51 degrees Fahrenheit shall weigh 12—13 of an equal measure of distilled water. Taking water at 51 degrees Fahrenheit as unity, the specific gravity of "proof spirit" at 51 degrees Fahrenheit is 0.92308. When such spirit is raised to the more usual temperature of 60 degrees Fahrenheit, the specific gravity is 0.91984. To calculate the quantity of spirits at proof in a given quantity of spirit over or under proof strength, multiply the quantity of spirit by the number of degrees of strength of the spirit, and divide the product by 100. The number of degrees of strength of any spirit is 100 plus the number of degrees overproof, or minus the number of degrees underproof.

Example :—

19.8 gallons of spirits at 64.5 overproof
 $100 \div 64.5 = 164.5$ proof strength.
 $164.5 \times 19.8 \div 100 = 32.571$
 taken as 32.5 gallons at proof.

ON THE POSSIBILITY OF MAKING SPECIAL REPORTS MORE AVAILABLE THAN AT PRESENT.*

THE Committee recommend :—

1. That at the close of each annual meeting of the Sectional Committee shall request its secretaries to compile a list of the Special Reports, other than those of Standing Committees, which have been presented to the Section during the previous five years, and which have been published *in extenso*, this list (see Appendix) to include those Reports of the character specified which have been presented at the annual meeting just terminated.

2. That the secretaries of the Sectional Committee be requested to forward copies of the list to the secretaries of the Chemical Societies of London and Berlin, with the suggestion that the councils of these bodies might be disposed to bring such Reports to the notice of Fellows by inserting the references in one of the issues of their publications.

* Report of the Committee, consisting of Mr. W. A. Shenstone (Chairman), Dr. M. O. Forster (Secretary), Prof. E. Divers, Prof. W. J. Pope, and Dr. A. W. Crossley. Read before the British Association (Section B), Southport Meeting, 1903.

Appendix.

List of Special Reports presented to Section B during 1898-1902, indicating the type of Special Report to which attention might be drawn in the manner indicated by the Committee :—

- 1900. "The Constitution of Camphor." By A. Lapworth.
- 1901. "Methods of Determining the Hydrolytic Dissociation of Salts." By R. C. Farmer.
- "On the Equilibrium Law as Applied to Salt Separation and to the Formation of Oceanic Salt Deposits." By E. F. Armstrong.
- 1902. "Hydro-aromatic Compounds with Single Nucleus." By A. W. Crossley.
- "Our Present Knowledge of Aromatic Diazo compounds." By G. T. Morgan.

THE CAUSE OF THE LUSTRE PRODUCED ON MERCERISING COTTON UNDER TENSION.*

By JULIUS HÜBNER, F.C.S., and WILLIAM J. POPE, F.R.S.

IT is generally supposed that the production of a lustre on treating stretched cotton-yarn with strong caustic soda is conditioned by only two factors—namely, by the simultaneous swelling and shrinking of the fibres. The authors show, however, that a third effect is essential to the production of any appreciable silky lustre; this consists in an uncoiling of the naturally twisted ribbon constituting the cotton-fibre.

On immersing a loose cotton-fibre in strong caustic soda on the microscope stage, it is seen to rapidly untwist, to swell, and at the same time, to shorten in length; the untwisting generally continues until the natural twist has nearly completely disappeared, after which the fibre presents the appearance of a round, irregularly curved rod, with a comparatively smooth surface. If the fibre is fixed at one end and treated with caustic soda, it twists either to the right or to the left, according as it was originally coiled towards the left or towards the right; in the most generally occurring case, that, namely, in which the fibre is coiled partly to the right and partly to the left, the untwisting attending the treatment with soda takes place first towards the left, and then towards the right or *vice versa*. If the fibre is prevented from contracting by being held at the two ends in a stretched condition it still untwists when treated with soda; since, however, the whole of the untwisting does not take place simultaneously, the untwisting of one part causes another part, which has already become unwound and attained the condition of a gelatinous rod to become tightly twisted in the opposite direction to: original twist.

The stretched fibre thus again acquires a corkscrew like appearance, part of the twist being right- and part left handed, with the difference, however, that whilst the raw fibre forms a twisted ribbon creased or folded at the turns treatment with soda converts it into a rod of circular cross-section which has been twisted whilst in a gelatinous state. The twisting of the fibre under these conditions results in the production on the rounded surface of spiral ridges possessing smooth curved contours, which reflect the light at all angles of incidence and reflection just as do the coils of a polished corkscrew. The fibre, therefore, becomes lustrous.

The high degree of transparency possessed by the cotton-fibre introduces difficulties into the microscopic examination of the changes referred to above. But although the fibre is amorphous, it is doubly refracting owing to internal strain; the authors therefore find it convenient to conduct the microscopic examination of the fibre between crossed Nicol prisms, and to accentuate the difference in tint of the

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

various parts by introducing a one-eighth wave-length retardation plate of mica between the Nicols in such a way that its principal directions make an angle of 45° with those of the prisms. This enables the internal canal, cracks in the surface, and differences in thickness to be made out with great ease. The correctness of the explanation now given of the lustre is shown by a series of photomicrographs taken in natural colours in elliptically polarised light under the conditions just referred to; the authors have to thank their colleague, Mr. Chas. W. Gamble, Director of the Photographic Department in the Manchester Municipal School of Technology, for having assisted the work by the production of these photographs. A further confirmation of the correctness of the conclusions now arrived at is afforded by the observation that whilst cotton-fibres mercerised loose have a practically circular cross-section, fibres treated under tension with soda show cross-sections shaped like polygons with rounded corners.

An independent proof of the authors' conclusions that the untwisting of the fibre is as essential a factor in the production of the gloss as are the swelling and the shrinking, is afforded by an examination of the action of reagents on cotton-yarn. Thus, hanks of a long staple yarn having a mean breaking strength of 417.4 ± 2.1 grms. were immersed loose in caustic soda (sp. gr. 1.342), and saturated barium mercuric iodide solution, and the following changes in the breaking load of the yarn and the lengths of the hanks were found to result:—

Caustic Soda.—Mean breaking load, 526.3 ± 3.8 grms. : shrinkage from 66.0 to 44.8 c.m.

Barium Mercuric Iodide.—Mean breaking load 526.6 ± 3.3 grms. ; shrinkage, from 66.0 to 48.9 c.m.

Although the shrinkage and the increase in the breaking load brought about by these two reagents is so nearly the same, yet on immersing hanks under tension in these solutions and washing whilst still under strain, the hank treated with soda acquires a brilliant lustre, whilst that treated with the iodide exhibits only a trace more lustre than the untreated yarn. The explanation of this result is found in the fact that caustic soda causes rapid untwisting of the fibre, whilst barium mercuric iodide does not cause untwisting.

The authors give a list of reagents which bring about two of the three effects shown to be essential to the production of lustre—namely, swelling, shrinking, and untwisting—and find that "lustreing" cannot be effected with such reagents; several solutions are known, however, which cause the three effects, and with the aid of such liquids the lustre can always be produced.

THE APPLICATION OF LOW TEMPERATURES TO THE STUDY OF BIOLOGICAL PROBLEMS.*

By ALLAN MACFADYEN, M.D.

THE cellular doctrine lies at the basis of modern biological research. Living matter, in its simple and complex conditions, consists essentially of protoplasm with a contained body, or nucleus. The two elements plasma and nucleus constitute the elementary organism—the cell. The lowest individual forms of life are represented by a single cell, and such unicellular organisms may be either of a vegetable or animal type. The cells in each instance exist as free living and independent organisms. The higher forms of life are built up of parts in which the structural unit remains the cell, despite the modifications the cell necessarily undergoes as a fixed element in the various tissues and organs. All phases of animal and plant life are demonstrably of cellular origin and organisation, and their vital manifestations represent the summed-up activities of cells. Every vital problem, therefore, is ultimately a cellular problem, and a direct study of the cell, in so far as may be possible, is the keynote upon the problem it is desired to investigate. A

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

histological technique aided by the microscope will naturally be employed where it is desired to study the relations of parts and the structural organisation of the tissues and their cellular elements. The soluble products of the living cell spontaneously present themselves for examination by chemical and other means. It is otherwise with regard to the agencies acting and the processes occurring within the confines of the cell. These are naturally beyond the range of the ordinary methods of observation. The essential processes of life are intra-cellular, and intimately bound up with the living substance of the cell, and of these but few data are possessed. The importance of the problems involved is as great as their investigation is difficult. The cell exercises its vital functions in virtue of a specific physical and chemical organisation of its molecular constituents. The ordinary methods of biological and chemical research modify or destroy this organisation, and do not admit of an intimate study of the normal cell constituents. For this purpose, it is essential to eliminate or to reduce to a minimum the influence of external modifying agents on the cell or its immediate products. An intra-cellular physiology can only be based on a direct study of intra-cellular constituents apart from their secretions and products. This, under ordinary circumstances is impossible with respect to actively functioning and intact cells. It is obvious, therefore, that the first desideratum is a suitable method of obtaining the cell plasma for experimental purposes, and it is only recently that this has been successfully accomplished. The most feasible means of procedure appeared to be the use of *mechanical* agents, which, whilst bringing the cell substance within the field of observation, would at the same time be least likely to affect its character and constitution. The method consists in a mechanical rupture of the cells and the release of their contents under conditions favouring the conservation of their properties. The first successful application of this description of method was made by Buchner in the particular instance of the yeast cell, and with brilliant results. The researches of Buchner were of wide biological significance, and were suggestive of much more than a cell-free alcoholic fermentation of sugars. They demonstrated the possibilities of the new methods with regard to more general vital problems. The Buchner process consisted in a mechanical trituration of the yeast cell with the aid of sand, and a subsequent filtration of the resultant mass under pressure through kieselguhr. The filtrate contained the expressed constituents of the yeast cell which were capable of passing through kieselguhr, and the product, in virtue of its fermentative properties, was termed "Zymase."

The writer and his colleagues have during the past four years been engaged in investigating the application of cognate methods to biological research. The advice and help generously afforded by Professor James Dewar materially forwarded the progress of the research.

It was considered that, by the employment of low temperatures, a disintegration of living cells might possibly be accomplished, and a wide field of inquiry opened to investigation in the biological laboratory. For this purpose the methods of mechanical trituration required refinement in several directions.

The conditions it was desired to fulfil were—a rapid disintegration of the fresh tissues and cells, an avoidance of heat and other modifying agents during the process, and an immediate manifestation of the cellular juices obtained.

It had likewise been noted that ordinary filter pressing through kieselguhr removed physiologically active substances from the cell juices. Liquid air appeared to be the most convenient means of obtaining the necessary cold, and it presented the advantage of a fluid freezing medium, in which the material to be manipulated could be directly immersed. The temperature of this reagent (about $-190^\circ\text{C}.$) would, in addition, prevent heat and chemical changes, whilst reducing the cells to a condition of brittleness favourable to their trituration without the addition of such substances as sand and kieselguhr, which might modify the composition of the resultant product.

The method, if successful, would meet the conditions desired for the subsequent study of the intra-cellular juices. It may be briefly stated that, by the application of low temperatures, a mechanical trituration of every variety of cell *per se* has been accomplished, and the fresh cell plasma obtained for the purpose of experiment. A number of control experiments have demonstrated that immersion in liquid air is not necessarily injurious to life—bacteria, for example, having survived a continuous exposure for six months to its influence. The actual trituration of the material is accomplished in a specially devised apparatus, which is kept immersed during the operation in liquid air.

The normal and diseased animal tissues have been treated in this manner, and their intra-cellular constituents obtained, e.g., epithelium, cancer tissues, &c.

Moulds, yeasts, and bacteria have been rapidly trituated under the same conditions, and the respective cell juices submitted to examination.

The severest test of the capabilities of the method was furnished by the bacteria—an order of cells for which the standard of measurement is the *mikron*. The experiments proved successful in every instance tested. The typhoid bacillus, for example, is trituated in the short space of two to three hours, and the demonstration has been furnished that the typhoid organism contains within itself a toxin. From these and other researches it has become evident that there exists a distinct class of toxins and ferments which are contained and operate within the cell or bacterium, in contradistinction to the now well-known class of toxins which are extra-cellular, i.e., extruded during life from the cell into the surrounding medium. To this latter class belongs the diphtheria toxin which has been so successfully used in the preparation of diphtheria antitoxin. A number of infective organisms do not produce appreciable extra-cellular toxins, and the search must therefore be made within the specific cells for the missing toxins to which the intoxication of the body in the course of the disease in question is probably due. The practical utility of investigating these intra-cellular toxins has already become evident in the preparation from the intra-cellular toxin of the typhoid bacillus of a cerum having antitoxic value as regards this toxin.

The experiments made with the pus organisms have already shown that intra-cellular toxins exist in this important order of disease germs.

The cell juices of other types of pathogenic bacteria, such as the tubercle and diphtheria bacillus, present characteristics of equal interest.

The application of low temperatures has aided the investigation of certain other biological problems.

The photogenic bacteria preserve their normal luminous properties after exposure to the temperature of liquid air. The effect, however, of a trituration at the same temperature is to abolish the luminosity of the cells in question. This points to the luminosity being essentially a function of the living cell, and dependent for its production on the intact organisation of the cell.

The rabies virus has not yet been detected or isolated, although regarded as an organised entity. The seat of the unknown rabies virus is the nervous system. If the brain substance of a rabid animal be trituated for a given length of time at the temperature of liquid air, its infective properties as regards rabies are abolished. This result appears to be a further indication of the existence in rabies of an organised virus.

The method described admits of a fresh study of the question of immunity from an intra-cellular standpoint.

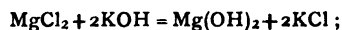
The intra-cellular juices of the white blood cells have been obtained, and tested with regard to bacteriolytic properties, and the natural protection that may thus be afforded to the body against the invasions of micro-parasites.

The application of low temperatures to the study of biological problems has furnished a new and fruitful method of inquiry.

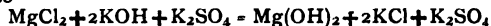
A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.*

By HARRISON EASTMAN PATTEN.

THE work on aluminium,[†] iron,[‡] zinc,[§] and chromium|| has shown that the action of their hydroxides in carrying down other substances into precipitation is chemical, and under certain conditions not proportional to the mass of precipitate. I have examined the action usually expressed by the equation—



also—



to ascertain whether magnesium hydroxide acts in a similar manner.

Solutions.

Solutions as described below were used in the work:—

1. For the magnesium solution, 20.2963 grms. of crystallised magnesium chloride was made up to 1 litre at 20°. This solution contained 0.0070 grm. chlorine, and 0.00308 grm. magnesium oxide per c.c.

2. A dilute solution of potassium hydroxide standardised by oxalic acid and gravimetrically. It contained 0.0261 grm. potassium hydroxide per c.c.

3. A dilute solution of sulphuric acid, standardised against the potassium hydroxide solution both volumetrically and gravimetrically (weighed as K_2SO_4). It contained 0.04206 grm. sulphuric acid per c.c.

As a preliminary step, the amount of potassium hydroxide required for exact precipitation of the magnesium in solution (1) was determined.

General Method.

The filtrates were analysed and the percentage of each constituent found deducted from that of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analysed directly, since washing or diluting the solution in which the precipitate is formed changes its composition. In the case of magnesium, the precipitated hydroxide is soluble in water.

A blank determination of the magnesium chloride was made:—50 c.c. magnesium chloride stock solution was made up to 500 c.c. at 20°, four portions were drawn off with a 50 c.c. pipette, and the magnesium oxide and chlorine determined in duplicate.

MgO	0.0207 grm.	0.0207 grm.
Cl	0.0040 "	0.0042 "

Experiments were now made with 44.24 c.c. sulphuric acid, neutralised to potassium sulphate by the equivalent amount of potassium hydroxide, and 50 c.c. stock solution of magnesium chloride as constant factors, the magnesium being precipitated by varying amounts of potassium hydroxide. The above constituents were made up to 500 c.c. at 20°, allowed to stand twenty minutes, well shaken, and four portions of mixed precipitate and solution drawn off with a dry 50 c.c. pipette, and labelled "totals." The solution and precipitate remaining was thrown upon a dry filter-paper, the clear filtrate brought back to 20°, and five portions drawn off with a 50 c.c. pipette, and labelled "filtrates."

The "totals" for magnesium oxide were re-dissolved by

* From the *Journal of the American Chemical Society*, vol. xxv., No. 2.

† "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide," *Am. Chem. Journ.*, viii., 23.

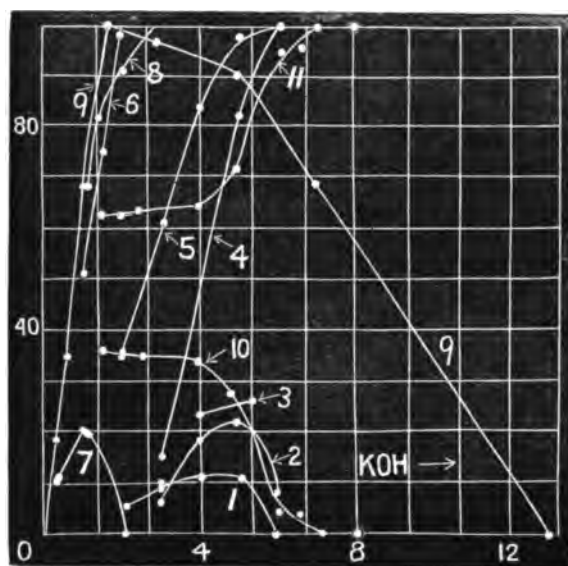
‡ "A Study of Ferric Hydroxide in Precipitation," *Ibid.*, xix., 312.

§ Unpublished.

|| Chromic Hydroxide in Precipitation, *Ibid.*, xviii., 608; also "Recherches sur le sulfate chromique, ses transformations et les acides complexes qui en dérivent," *Ann. Chem. Phys.*, 1893, vii., 4.

TABLE I.

Experiment.	KOH.	"Total" MgO.		"Filtrate" MgO.		"Precipitate" MgO.		"Total" Cl.		"Filtrate" Cl.		"Precipitate,"	
												Cl.	% MgO.
I.	2	0.02065 0.02071	0.0207	Only a trace.		0.0207	0.0036 0.0035	0.0036	0.0037 0.0040	0.0038	0.0000	100.00	
II.	6 (2)	0.1190 + 0.1190 -	0.1190	0.0026 0.0020	0.0023	0.1167	0.2082 0.2085	0.2084	0.2086 0.2088	0.2087	0.0000	98.06	
III.	6 (1½)	0.1174 0.1180	0.1177	0.0281 0.0276	0.0278	0.0899	0.2080 0.2085	0.2083	0.2081 0.2087	0.2084	0.0000	76.38	
<i>New Solution.</i>													
IV.	1½ + K ₂ SO ₄	0.1926 0.1927	0.1926	0.0480 0.04807	0.0480	0.1446	0.3445 0.3443	0.3444	0.3442 0.3438	0.3440	0.0004	75.07	
V.	1½	0.1928 0.1931	0.1929	0.0484 0.0481	0.0482	0.1447	0.3431 0.3432	0.3431	0.3427 0.3429	0.3428	0.0003	75.07	
VI.	1 + K ₂ SO ₄	0.1936 0.1942	0.1939	0.0958 0.0963	0.0960	0.0979	0.3430 0.3425	0.3427	0.3433 0.3429	0.3431	0.0000	50.46	
VII.	1	0.1941 0.1940	0.1940	0.0968 0.0966	0.0966	0.0974	0.3426 0.3429	0.3427	0.3427 0.3426	0.3426	0.0001	50.46	



hydrochloric acid in some excess, ammonia added to alkaline reaction, and the magnesium precipitated cold as magnesium ammonium phosphate, and weighed as pyrophosphate.

The "totals" for chlorine were re-dissolved by nitric acid, precipitated hot with silver nitrate solution, and the magnesium removed by a wash-water containing 25 c.c. concentrated nitric acid and 0.1 grm. silver nitrate per litre. The chlorine was then weighed as silver chloride.

The "filtrates" for magnesium oxide and chlorine were analysed in the same manner as the "totals." As in the work with aluminium, chromium, iron, and zinc, it was assumed that resolution by hydrochloric or nitric acid would liberate any constituents carried down in the precipitation with potassium hydroxide.

It was considered unnecessary to determine the potassium oxide in the "totals" and "filtrates," for two reasons:—First, because in all the foregoing work in this line no carrying down of potassium was observed short of resolution in the alkali; second, the negative results of the work on magnesium oxide, chlorine, and sulphur trioxide in this investigation indicate the absence of such action.

No good method of separating the magnesium oxide from the sulphur trioxide in "totals" and "filtrates" being available, two different methods were used to ascertain whether the sulphur trioxide enters into the reaction.

1. The amount of magnesium oxide precipitated in presence of *potassium sulphate* by a definite amount of potassium hydroxide, should be greater than the amount precipitated in absence of the sulphate—if *sulphur trioxide enters into the reaction.**

2. Magnesium oxide or chloride should be carried down into precipitation by barium sulphate. The four elements already mentioned show this reciprocal action, as does also manganese, of which I shall speak later.

Experiment I.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$, using 50 c.c. of magnesium chloride solution to 22.2 c.c. potassium hydroxide solution. No potassium sulphate was introduced here, since the object was to determine if chlorine were carried down into precipitation by the magnesium hydroxide. No chlorine was found in the precipitate (see Table I., Exp. I.). A trace of magnesium was obtained in the filtrate by further addition of potassium hydroxide, showing that magnesium chloride is not completely precipitated by 2 molecules of potassium hydroxide. As the mass of precipitate was so small, for this concentration, and as "adhesion" in the cases of chromium, iron, aluminium, and zinc hydroxides is more marked in concentrated solutions,

* Series II., "Chromic Hydroxide in Precipitation," *loc. cit.*, "A Study of Ferric Hydroxide in Precipitation" *loc. cit.*

the next two experiments were made up each with six 50 c.c. portions of magnesium chloride solution instead of one 50 c.c. portion as in this experiment.

Experiment II.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$ (see Table I., Exp. II., for results). This shows no chlorine carried down into precipitation. Since adhesion is more marked at incomplete precipitation than at complete precipitation, in the next experiment I used $1\frac{1}{2}$ KOH.

Experiment III.—The system was made up according to the equation $MgCl_2 + 1\frac{1}{2}KOH = ?$ (see Table I., Exp. III., for results). Here again no chlorine is carried down by the precipitate.

The stock supply of magnesium chloride being now exhausted, a new solution (4) was made up:—203 grms. $MgCl_2 + 6H_2O$ were dissolved in water, and diluted to 1000 c.c. of solution at 20° C. One 50 c.c. portion was drawn off, and made up to 500 c.c. at 20° C. Of this solution each 50 c.c. contained:—

MgO	0.1926 grm.	0.1925 grm.
Cl.	0.3445 "	0.3440 "

For 50 c.c. of stock solution of magnesium chloride (4), 212.5 c.c. potassium hydroxide were required to precipitate completely the magnesium. The calculated amount of potassium hydroxide was 207 c.c.

Now the attempt was made to ascertain if sulphur trioxide is carried down into precipitation. As was stated in "General Method," no good means of separation being at hand, a difference method was resorted to. The work on chromium and iron showed that in a partially precipitated system (which had been filtered or allowed to settle) further precipitation was caused by the addition of a little sulphate solution, and in some cases* no definite precipitate was obtained unless some soluble sulphate was present. From this influence of sulphur trioxide on the amount of hydroxide formed at fractional precipitation, I assume that if sulphur trioxide is carried down into precipitation by magnesium hydroxide, the amount of magnesium hydroxide precipitated by, say, 1.5 molecules of potassium hydroxide will be greater in the presence of sulphur trioxide than in its absence. If then, the amount of magnesium hydroxide precipitated by 1.5 molecules of potassium hydroxide is the same with and without sulphur trioxide present, I conclude that no adhesion takes place.

For results see Experiments IV., V., VI., VII., Table I., and the accompanying plate, curve 6.

The same amount of magnesia is precipitated in Experiment IV. with potassium sulphate present as in Experiment V. with potassium sulphate absent; likewise in Experiments VI. and VII. Since no sulphur trioxide is carried down into precipitation at these fractional points it was considered unnecessary to try an experiment at complete precipitation, inasmuch as the other elements worked with show their greatest "adhesion" activity at these points. Further, since magnesium gives a definite precipitate at the fractional points in absence of sulphur trioxide, it ought to carry down chlorine into precipitation if it exercises the property of "adhesion"; Experiments I., II., and III., show no chlorine carried down.

Experiment VIII.—It was determined that magnesium hydroxide precipitated from magnesium chloride by potassium hydroxide in aqueous solution does not re-dissolve in excess of potassium hydroxide.

Experiment IX.—Twelve different barium sulphate determinations which had been made from solutions containing magnesium chloride, potassium, sulphate, and hydrochloric acid by addition of barium chloride were treated as follows:—Fused with sodium carbonate, the alkali washed out with water, the insoluble barium carbonate dissolved in hydrochloric acid, re-precipitated by ammonium carbonate to remove the barium, and the filtrate tested for magnesium

by sodium hydrogen phosphate. Not a trace of magnesium was found.

Discussion.

These results may be summarised thus:—(1) Magnesium hydroxide does not carry down into precipitation with it either chlorine or sulphur trioxide. (2) Barium sulphate does not carry down into precipitation either magnesium oxide or chloride. (3) More than the theoretical amount of potassium hydroxide is required to completely precipitate magnesium hydroxide from a magnesium chloride solution in water at the concentration and temperature studied. On this last point more work should be done.

(To be continued).

FREEZING-POINT CURVES FOR BINARY SYSTEMS.*

By JAMES C. PHILIP, M.A., B.Sc., Ph.D.

WHEN a liquid mixture of two components is slowly cooled, separation of solid will take place at some temperature. For complete interpretation of the phenomena, it is necessary to know not only (1) this temperature of initial freezing, but also (2) the composition of the separating solid, and (3) the composition of the liquid with which this solid is in equilibrium. The varying character of the relationship between (2) and (3) is best seen by plotting the one against the other in a square diagram. It is found then that the experimentally known cases fall into one or other of two classes, according as the composition of the separating solid varies continuously with that of the liquid from which it separates, or is for certain ranges of concentration definite and constant. To the former class belong systems of components that form mixed crystals; to the latter class belong systems of components that, forming no mixed crystals, may form definite compounds.

If now attention is confined to the latter class, and the freezing-point curves (that is, the curves showing the relationship between the temperature of initial freezing and the composition of the liquid) are considered for such systems, experimental work shows that to each range of concentration over which the composition of the separating solid is definite and constant, there corresponds a branch of the freezing-point curve. There are always at least two such branches over which separation of the pure components takes place, and there may be one or more intermediate branches with a maximum or summit over which separation of definite compounds takes place (see, for example, Guthrie, *Phil. Mag.*, 1884, xvii., 643; Dahms, *Wied. Ann.*, 1895, liv., 486; Stortenbeker, *Zeit. Physikal. Chem.*, x., 194; Heycock and Neville, *Phil. Trans.*, A., cxciv., 201; Kuriloff, *Zeit. Physikal. Chem.*, 1897, xxiii., 547, 673; Philip, *Journ. Chem. Soc.*, 1903, lxxxiii., 814). The composition at a summit-point on a freezing-point curve is exactly that of the corresponding straight line on the square diagram referred to above, and thus the occurrence of an intermediate mound on the freezing-point curve is to be taken as evidence that the components form a compound, the composition of which is given by the summit-point. It is further to be observed that the various branches of a freezing-point curve cut each other at an angle, as shown by the fact that a branch can be continuously realised beyond its point of section with another branch; illustrations of this are found in Roozeboom's work on the hydrates of ferric chloride and in the author's study (*loc. cit.*) of the freezing-point curve for mixtures of phenol and *n*-naphthylamine.

Beyond these general characteristics of freezing-point curves, there are certain special features that are of interest, and that have received illustration in some recent work. For example, there may be an intermediate branch that

* Fractional precipitation of chromium chloride by less than three molecules of potassium hydroxide. See "Chromic Hydroxide in Precipitation," *loc. cit.*

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

does not reach a summit, pointing to the formation of a compound that is unstable at its own melting-point. A case in point is supplied by Donnan and Burt's work on the hydrates of lithium nitrate (*Journ. Chem. Soc.*, 1903, lxxxiii., 335), and to a certain extent by the author's work on the freezing-point curve for phenol and urea. These two form a compound containing one molecule of urea to two of phenol, and the freezing-point curve shows a corresponding branch that just reaches a summit, where it is cut by another branch along which separation of urea takes place. The passage from one branch to another, as in this case of phenol and urea, is marked by an obvious change in the character of the primary crystallisation, and by the existence of secondary or eutectic freezing-points on the same level as the intersection of the two branches.

The freezing-point curve becomes especially interesting when the two components form a dimorphous compound. While the general rule still holds that for each solid form there is a branch of the freezing-point curve, the one branch in this case is found to envelope the other, the two summit-points occurring at the same composition. The only cases where this bearing of dimorphism on the freezing-point curve has been studied are Stortenbeker's investigation (*loc. cit.*) of the freezing-point curve of iodine and chlorine, and the author's work (*loc. cit.*) on that of phenol and *p*-toluidine. In this latter case a compound is formed which exists in two modifications (as plates and needles), and when a liquid mixture containing from 30–60 molecular per cent of *p*-toluidine is allowed to cool, a primary crystallisation of plates is observed, the freezing-point being obtained in the usual manner. Presently a transformation of the plates into the more stable needles takes place; this is accompanied by a rise of temperature, and a second freezing-point is obtained, generally about 1.5° higher than the one first observed. These observations may be repeated with mixtures of different composition, and thus two branches of the freezing-point curve are obtained, the one of which, as has been said, envelopes the other.

THE INFLUENCE OF SMALL QUANTITIES OF WATER IN BRINGING ABOUT CHEMICAL REACTION BETWEEN SALTS.*

By EDGAR PHILIP PERMAN, D.Sc.

MANY experimenters have investigated the influence of traces of moisture in reactions between gases, but so far as I am aware no one has hitherto made similar experiments with solids.

The substances chosen for experiment were salts of lead or mercury, and salts of potassium, usually the iodide, which would show the occurrence and progress of a reaction by a colour change.

a. Experiments with Lead Chloride and Potassium Iodide.—Equivalent quantities of the two salts were dried over strong sulphuric acid in a suitable apparatus, and then mixed; it was found that after forty-eight hours' drying no visible change took place on mixing the salts, but on keeping the mixture for a week (in a sealed flask) a faint yellow colour appeared, which gradually deepened, until after some months it became a bright yellow.

Attempts were made to discover how much water was necessary in order to make the reaction immediately visible; the results were not very concordant, but indicated about 0.5 m.grm. as the amount necessary in the conditions of the experiment, viz. 2 grms. of potassium iodide and an equivalent quantity of lead chloride were mixed in a glass flask of about 100 c.c. capacity.

b. Experiments with other Lead Salts and Potassium Iodide.—Lead formate and lead nitrate were found to act in a similar way to the chloride.

Lead sulphate reacts much more slowly, although exposed to the air, while the carbonate and the oxide react very slowly indeed.

c. Experiments with Mercuric Chloride and Potassium Iodide.—Mercuric chloride and potassium iodide treated in exactly the same way as already described gave a strong red colouration on mixing; the same result was obtained when commercial phosphoric anhydride was used as a drying agent. By drying with specially prepared phosphoric anhydride, however, the mixture obtained has been kept for some months without change.

d. Other Experiments with Mercuric Salts.—Mercuric cyanide showed no reaction with potassium iodide.

Mercuric chloride and potassium chromate reacted very slowly, although exposed to the air.

Discussion of Results.—There is no reason for thinking that these reactions take place in any way essentially different from similar reactions in solution, and I believe that the only difference is the extreme slowness of the reaction. It is noteworthy that the velocity of the reaction between mercuric chloride and potassium iodide is enormously greater than that between lead chloride and potassium iodide when dried in the same way. The factors to which this difference may be referred are (1) solubility, (2) volatility, (3) degree of ionisation, (4) specific reaction velocity. We will consider these in order.

1. Mercuric chloride is about ten times as soluble as lead chloride in cold water, but this alone would not account for the difference; e.g., mercuric cyanide is still more soluble, but does not react at all.

2. Judging from the boiling-points, mercuric chloride would appear to be more volatile than lead chloride, the boiling-point of the former being 300° C., and that of the latter about 900° C.; but I find that on aspirating air over each salt, and then over potassium iodide, the vapour from the lead chloride affects the potassium iodide much the sooner.

The difference in the speed of the two reactions (*a* and *c*) cannot therefore be caused by the difference in volatility.

3. The degree of ionisation cannot be the cause of the difference noted, for mercuric chloride is known to be very slightly ionised in solution, while lead chloride may be taken as completely ionised.

4. The specific reaction velocity appears to be the real determining factor, and the reaction is probably of the form $AB + CD = AD + BC$. If it is only free ions that react (which seems to me improbable), then the velocity of ionisation in the case of mercuric chloride must be extremely great.

There may also be other factors at present unknown.

CORRESPONDENCE.

COSMICAL RADIO-ACTIVITY.

To the Editor of the Chemical News.

SIR,—In a paper entitled "Cosmical Radio-activity" read before the British Association, and reprinted in the *CHEMICAL NEWS* (vol. lxxxviii., p. 166), Mr. Arthur Schuster suggests that radio-activity may be a common property of all matter—the apparently inactive metals possessing it in so small a degree that our power of observation is insufficient to detect it. May I be allowed to point out that this view is not new, but has already been put forward and discussed by me in your columns more than two-and-a-half years ago; *vide* *CHEMICAL NEWS*, March 15, 1901 (vol. lxxxiii., p. 130), and again on May 2, 1902 (vol. lxxxv., p. 205)? Since that time, of course, an enormous extension of our knowledge has been made concerning radio-activity, but I see no cause to alter the views then put forward, except that, in the last paper referred to above, I have probably exaggerated the effect of temperature.—I am, &c.,

GEOFFREY MARTIN.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

NOTICES OF BOOKS.

Foods: Their Composition and Analysis. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., &c., and MEREDITH WYNTER BLYTH, B.A. (Cantab), B.Sc. (Lond.), F.I.C., F.C.S., &c. Fifth Edition. London: Charles Griffin and Co., Ltd. 1903.

THE fifth edition of this standard work on Food Analysis has been to a great extent re-written, some portions having been greatly enlarged, while others have been condensed or omitted. Chapters on the detection and determination of arsenic and the bacteriology of water, &c., have been added, and in every respect the text has been brought up to date; the account of the present state of the law in England with regard to the adulteration of food, and the text of Adulteration Acts, will be found very useful by public analysts. The position of this work is thoroughly established, and it is well known and properly regarded as almost indispensable by all engaged in analytical chemistry, so that it is unnecessary to do more than indicate the special features of this latest edition, which contains much fresh useful matter.

Ausgewählte Methoden der Analytischen Chemie. Zweiter Band. ("Select Methods of Analytical Chemistry." Volume II.). By Prof. Dr. A. CLASSEN. Braunschweig: Friedrich Vieweg und Sohn. 1903.

THE second volume of this book contains an account of the application of the methods of analytical chemistry to the non-metallic elements and their compounds. The most modern and accurate methods of analysis, both qualitative and quantitative, are given with sufficient explicitness and detail for the student to carry out all the operations described without further assistance. Special applications of the various processes are mentioned, and technical methods are also discussed. The analysis of water is particularly fully described, and the chapters on the treatment of explosives may also be mentioned as excellent; the elementary analysis of organic compounds is included among the subjects dealt with. This work is undoubtedly one of the most complete of its class extant, and can be thoroughly recommended.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 11, September 14, 1903.

Simplicity of the Spectra of Cathode Light in Gases containing Nitrogen and Carbon.—H. Deslandres.—In the simple gases containing nitrogen and carbon, cathode light is remarkably simple, and this property can be further studied by examining the intimate nature of the phenomenon. In 1890 the author investigated the reasons upon which the structure and chemical formula of illuminating gases depend, also the number and the grouping of the rays whose repetition gives rise to the spectrum bands. The numerous spectra of carbon and nitrogen which are examined are due to the different allotropic states of the simple bodies or their compounds with the elements of water. Under these conditions the spectra of the positive pole formed by the repetition of multiple rays correspond to molecules containing several atoms; the negative spectra, on the contrary, are due to a single atom. It may also be stated that the cathode light, which, when feeble, ionises gases, when stronger will also illuminate them, giving band spectra, and, by so doing, decomposes them into their simplest chemical elements. When the electric spark becomes more powerful the bands disappear, giving place to lines.

Action of a Trace of Water on the Decomposition of Alkaline Hydrides by Acetylene.—Henri Moissan.—The author's present series of experiments investigate the action of a trace of water on a chemical reaction. They correspond to those experiments which he has already described *à propos* of the synthesis of formates by means of carbon dioxide and the hydrides. Dry acetylene gas does not act on potassium hydride, except at temperatures above $+42^{\circ}$. If the gas, however, contains a trace of water, this latter modifies the conditions of the reaction, so that it takes place at ordinary temperatures. The author attributes this change to the evolution of heat, which, once started at a particular point, causes an elevation of temperature which raises the hydride to $+42^{\circ}$, and so causes the reaction to take place.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Separation of Methyl from Ethyl Alcohol.—I should be very much obliged if some reader would supply a description of a method or methods (not necessarily commercial) by which methyl may be separated from ethyl alcohol in a simple mixture of the two alcohols, with a view of recovering the latter alcohol; and also a method of detecting the presence of methyl alcohol in the presence of its next higher homologue.—S. J. HILL, New South Wales.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "Report on the Recent Foraminifera of the Malay Archipelago" (Part XV), by Fortescue W. Millett, F.R.M.S. Exhibition of Drawings and Slides of British Hydrachnidæ, by C. D. Soar, F.R.M.S.

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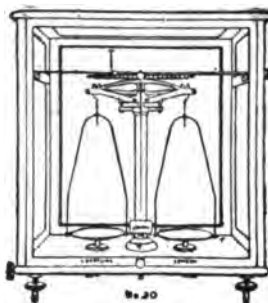
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2291.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 198).

CHAPTER III. (continued).¹

POLONIUM is particularly well adapted to the study of α -rays, because the specimens which we possess emit no other kind of rays. I made a preliminary series of experiments with extremely active recently prepared specimens of polonium. I found the absorbability of the rays to increase with increase of thickness of the matter traversed. This singular law of absorption is contrary to that known for other kinds of radiation.

I employed for this research our apparatus for the determination of electrical conductivity arranged in the following manner:—

The two plates of a condenser, P P and P' P' (Fig. 8), are horizontally disposed in a metallic box, B B B, connected to earth. The active body, A, placed in a thick metallic box, C C C, connected with the plate P' P', acts upon the air of the condenser across a metallic sheet, T; the rays which pass through the sheet are alone utilised for producing the current, the electric field being limited by the sheet. The distance, A T, of the active body from the sheet may be varied. The field between the plates is established by means of a battery. By placing in A upon the active body different screens, and by adjusting the distance A T, the absorption of rays which travel long or short distances in the air may be determined.

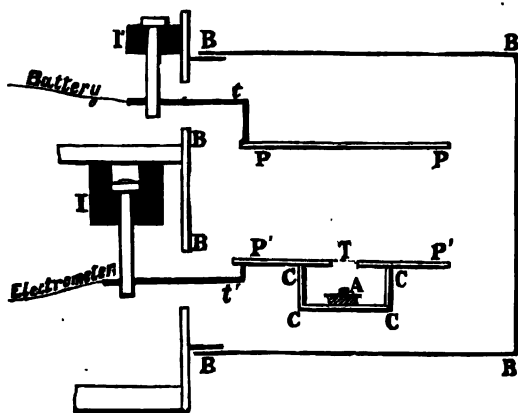


FIG 8.

The following are the results obtained with polonium:—

For a certain value of the distance A T (4 c.m. and more), no current passes; the rays do not penetrate the condenser. When the distance A T is diminished, the appearance of the rays in the condenser is manifested somewhat suddenly, a weak current changing to one of considerable strength for a slight diminution of distance; the current then increases regularly as the active body continues to approach the sheet T.

When the active body is covered with a sheet of aluminium $\frac{1}{10}$ m.m. thick, the absorption produced by the lamina becomes greater, the greater the distance A T.

If a second similar lamina of aluminium be placed upon

the first, each absorbs a fraction of the radiation it receives, and this fraction is greater for the second lamina than for the first.

In the following table I have represented in the first line the distances in centimetres between the polonium and the sheet T; in the second line the percentage of the rays transmitted by a sheet of aluminium; in the third line the percentage of the rays transmitted by two sheets of the same aluminium:—

Distance A T	3'5	2'5	1'9	1'45	0'5
Percentage of rays transmitted by one lamina	0	0	5	10	25
Percentage of rays transmitted by two laminæ	0	0	0	0	0'7

In these experiments the distance of the plates, P and P', was 3 c.m. We see that the interposition of the aluminium screen diminishes the intensity of the radiation to a greater degree at further distances than at nearer distances.

This effect is still more marked than the preceding figures seem to indicate. For a distance of 0'5 c.m. 25 per cent represents the mean penetration for all the rays which pass beyond this distance. If, for example, only those rays between 0'5 c.m. and 1 c.m. be comprehended, the penetration would be greater. And if the plate P be placed at a distance of 0'5 c.m. from P' the fraction of the radiation transmitted by the aluminium lamina (for A T = 0'5 c.m.) is 47 per cent, and through two laminæ it is 5 per cent of the original radiation.

I have recently performed a second series of experiments with these same specimens of polonium, the activity of which was considerably diminished, the interval of time between the two series of experiments being three years.

In the former experiments, polonium nitrite was used; in the latter, the polonium was in the state of metallic particles obtained by fusing the nitrite with potassium cyanide.

I found that the radiation of polonium had preserved its essential characteristics, and I discovered new results. The following, for different values of the distance A T, are the fractions of the radiation transmitted by a screen composed of four superposed very thin leaves of beaten aluminium.

Distance A T, in centimetres	0	1'5	2'6
Percentage of rays transmitted by the screen	76	66	39

I also found that the fraction of the radiation absorbed by a given screen increases with the thickness of the material already traversed by the radiation, but this only occurs after the distance A T has reached a certain value. When this distance is zero (the polonium being in contact with the sheet, either outside or inside the condenser), it is observed that with several similar superposed screens, each absorbs the same fraction of the radiation it receives; otherwise expressed, the intensity of the radiation diminishes therefore according to an exponential law as a function of the thickness of the material traversed, as in the case of homogeneous radiation transmitted by the lamina without changing its nature.

The following numerical results are given with reference to these experiments:—

For a distance A T equal to 1'5 c.m. a thin aluminium screen transmits the fraction 0'51 of the radiation it receives when acting alone, and the fraction 0'34 of the radiation it receives when it is preceded by another similar screen.

On the contrary, for a distance A T equal to zero, the same screen transmits in both the cases considered the same fraction of the radiation it receives, and this fraction is equal to 0'71; it is therefore greater than in the preceding case.

The following numbers indicate for a distance A T equal to 0 and for a succession of thin superposed screens, the ratio of the radiation transmitted to the radiation received for each screen:—

* Thesis presented to the Faculté des Sciences de Paris.

Series of nine very thin copper leaves.	Series of seven very thin aluminium leaves.
0.72	0.69
0.78	0.94
0.75	0.95
0.77	0.91
0.70	0.92
0.77	0.93
0.69	0.91
0.79	
0.68	

Taking into account the difficulties of the manipulation of very thin screens and of the superposition of screens in contact, the numbers of each column may be looked upon as constant; the first number only of the aluminium column indicates a greater absorption than that indicated by the following numbers.

The α -rays of radium behave similarly to the rays of polonium. These rays may be investigated almost isolated by deflecting to one side the β -rays with the magnetic field; the γ -rays seem of slight importance in comparison with the α -rays. The operation can only be carried on at some distance from the source of radiation. The following are the results of an experiment of this kind. The fraction of the radiation transmitted by a lamina of aluminium 0.01 m.m. thick is measured; this screen was placed always in the same position, above and at a little distance from the source of radiation. With the apparatus of Fig. 5, the current produced in the condenser for different values of the distance AD is observed, both with and without the screen:—

Distance AD	6.0	5.1	3.4
Percentage of rays transmitted by the aluminium	3	7	24

The rays which travel furthest in the air are those most absorbed by the aluminium. There is therefore a great similarity between the absorbable α -rays of radium and the rays of polonium.

The deflected β -rays and the undeflected penetrating γ -rays are, on the contrary, of a different nature. The experiments, notably of MM. Meyer and von Schweidler, clearly show that, considering the radiation of radium as a whole, the penetrating power of this radiation increases with the thickness of the material traversed, as is the case of Röntgen rays. In these experiments the α -rays produce scarcely any effect, being for the most part suppressed by very thin absorbent screens. Those which penetrate are, on the one hand, β -rays more or less scattered; on the other hand, γ -rays, which appear similar to Röntgen rays.

The following are the results of some of my experiments on the subject:—

The radium is enclosed in a glass vessel. The rays, which emerge from the vessel, traverse 30 c.m. of air, and are received upon a series of glass plates, each of thickness 1.3 m.m.; the first plate transmits 49 per cent of the radiation it receives, the second transmits 84 per cent of the radiation it receives, the third transmits 85 per cent of the radiation it receives.

In another series of experiments the radium was enclosed in a glass vessel placed 10 c.m. from the condenser which received the rays. A series of similar screens of lead each 0.115 m.m. thick were placed on the vessel.

The ratio of the radiation transmitted to the radiation received is given for each of the successive screens by the following numbers:—

0.40	0.60	0.72	0.79	0.89	0.92	0.94	0.94	0.97
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For a series of four screens of lead, each of which was 1.5 m.m. thick, the ratio of the radiation transmitted to the radiation received was given for the successive screens by the following numbers:—

0.09	0.78	0.84	0.82
------	------	------	------

The results of these experiments shows that when the thickness of the lead traversed increases from 0.1 m.m. to 6 m.m., the penetrating power of the radiation increases.

I found that, under the experimental conditions mentioned, a screen of lead 1.8 c.m. thick transmits 2 per cent of the radiation it receives; a screen of lead 5.3 c.m. thick transmits 0.4 per cent of the radiation it receives. I also found that the radiation transmitted by a thickness of lead of 1.5 m.m. consists largely of rays capable of deflection (cathode order). The latter are therefore capable of traversing not only great distances in the air, but also considerable thicknesses of very absorbent solids, such as lead.

In investigating with the apparatus of Fig. 2 the absorption exercised by an aluminium screen 0.01 m.m. thick upon the total radiation of radium, the screen being always placed at the same distance from the radiating body, and the condenser being placed at a variable distance, AD, the results obtained are the sum of those due to the three groups of the radiation. At a long distance the penetrating rays predominate, and the absorption is slight; at a short distance the α -rays predominate, and the absorption becomes less with nearer approach to the substance; for an intermediate distance the absorption passes through a maximum and the penetration through a minimum.

Distance AD	7.1	6.5	6.0	5.1	3.4
Percentage of rays transmitted by aluminium ..	91	82	58	41	48

Certain experiments made in connection with absorption always demonstrate a certain similarity between the α -rays and the β -rays. Thus it was that M. Becquerel discovered that the absorbent action of a solid screen upon the β -rays increases with the distance of the screen from the source, such that if the rays are subjected to a magnetic field, as in Fig. 4, a screen placed in contact with the source of radiation allows a larger portion of the magnetic spectrum to be in evidence than does the same screen placed upon the photographic plate. This variation of the absorbent effect of the screen with the distance of the screen from the source is similar to that which occurs with the α -rays; this has been verified by MM. Meyer and von Schweidler, who operated by means of the fluoroscopic method; M. Curie and I observed the same fact when working by the electrical method. However, when the radium is enclosed in a glass tube and placed at a distance from the condenser, which is itself enclosed in a thin aluminium box, it becomes a matter of indifference whether the screen be placed against the source or against the condenser; the current obtained is the same in both cases.

The investigation of the α -rays led me to the reflection that these rays behave like projectiles having a certain initial velocity, and which lose their force on encountering obstacles. These rays, moreover, travel by rectilinear propagation, as has been shown by M. Becquerel in the following experiment:—Polonium emitting rays was placed in a very narrow straight cavity hollowed in a sheet of cardboard. Thus a linear source of radiation was produced. A copper wire, 1.5 m.m. in diameter, was placed parallel and opposite to the source at a distance of 4.9 m.m. Beyond was placed a parallel photographic plate at a distance of 8.65 m.m. After an exposure of ten minutes, the geometric shadow of the wire was perfectly reproduced, with a narrow penumbra corresponding to the size of the source. The same experiment succeeded equally well when a double leaf of beaten aluminium was placed against the wire, through which the rays must pass.

There are therefore rays capable of giving perfect geometric shadows. The experiment with the aluminium shows that these rays are not scattered in traversing the screen, and that this screen does not give rise to any noticeable extent to secondary rays similar to the secondary rays of the Röntgen rays.

The experiments of Mr. Rutherford show that the projectiles which constitute the α -rays are deflected by a magnetic field, as if they were positively charged. The deflection in a magnetic field becomes less as the product $\frac{mv}{e}$ becomes greater; m being the mass of the particle, v its velocity, and e its charge. The cathode rays of radium

are but slightly deflected, because their velocity is enormous; they are, on the other hand, very penetrating, because each particle has a very small mass together with a great velocity. But particles which, with an equal charge and a less velocity, have a greater mass, would be also only slightly influenced by the action of the field, and would give rise to very absorbable rays. From the results of Mr. Rutherford's experiments, this seems to take place in the case of the α -rays.

The penetrating γ -rays appear to be of quite another nature, and similar to Röntgen rays.

We have now seen how complex a phenomenon is the radiation of radio-active bodies. The difficulties of investigation are increased by the question as to whether the radiation undergoes a merely selective absorption on the part of the material, or whether a more or less radical transformation.

Little is so far known with regard to this question. If the radiation of radium be regarded as containing rays both of the cathode and Röntgen species, it might be expected to undergo transformations in traversing screens. It is known:—Firstly, that cathode rays emerging from a Crookes tube through an aluminium window are greatly scattered by the aluminium; and, further, that the passage through the screen entails a diminution of the velocity of the rays. In this way, cathode rays with a velocity equal to 1.4×10^{10} c.m. lose 10 per cent of their velocity in passing through 0.01 m.m. of aluminium. Secondly, cathode rays on striking an obstacle give rise to the production of Röntgen rays. Thirdly, Röntgen rays, on striking a solid obstacle, give rise to the production of secondary rays, which partly consist of cathode rays.

The existence, by analogy, of all these preceding phenomena may therefore be predicted for the rays of radio-active substances.

In investigating the transmission of polonium rays through a screen of aluminium, M. Becquerel observed neither the production of secondary rays nor any transformation into cathode rays.

I endeavoured to demonstrate a transformation of the rays of polonium by using the method of interchangeable screens. Two superposed screens, E_1 and E_2 , being traversed by the rays, the order in which they are traversed should be immaterial if the passage through the screens does not transform the rays; if, on the contrary, each screen transforms the rays during transmission, the order of the screens is of moment. If, for example, the rays are transformed into more absorbable rays in passing through lead, and no such effect is produced by aluminium, then the system lead-aluminium will be more opaque than the system aluminium-lead; this takes place with Röntgen rays.

My experiments show that this phenomenon is produced with the rays of polonium. The apparatus employed was that of Fig. 8. The polonium was placed in the box, cccc, and the absorbing screens, of necessity very thin, were placed upon the metallic sheet, T.

Screens employed.	Thickness.	Current observed.
	M.m.	
Aluminium	0.01	17.9
Brass	0.005	
Brass	0.005	6.7
Aluminium	0.01	
Aluminium	0.01	150
Tin	0.005	
Tin	0.005	125
Aluminium	0.01	
Tin	0.005	13.9
Brass	0.005	
Brass	0.005	4.4
Tin	0.005	

The results obtained prove that the radiation is modified in passing through a solid screen. This conclusion accords with the experiments in which, of two similar superposed metallic screens, the first is less absorbent than the second. From this it is probable that the transforming action of a screen increases with the distance of the screen from the source. This fact has not been verified, and the nature of the transformation has not been studied in detail.

I repeated the same experiments with a very active salt of radium; the result was negative. I only observed insignificant variations in the intensity of the radiation transmitted with interchange of the order of the screens. The following systems of screens were experimented with:—

Aluminium, thickness		0.55	m.m.
"	"	0.55	"
"	"	0.55	"
"	"	1.07	"
"	"	0.55	"
"	"	1.07	"
"	"	0.15	"
"	"	0.15	"
"	"	0.15	"
Platinum,	"	0.01	"
Lead,	"	0.1	"
Tin,	"	0.005	"
Copper,	"	0.05	"
Brass,	"	0.005	"
"	"	0.005	"
Platinum,	"	0.01	"
Zinc,	"	0.05	"
Lead,	"	0.1	"

The system lead-aluminium was slightly more opaque than the system aluminium-lead, but the difference was not great.

Thus, I was unable to discover an appreciable transformation of the rays of radium. However, in various radiographic experiments, M. Becquerel observed very intense effects due to scattered or secondary rays, emitted by solid screens which received radium rays. Lead seemed to be the most active substance in this respect.

(To be continued).

Action of the Hydrated Oxide of Cadmium on the Ammoniacal Salts.—H. Grossmann.—While examining the action of the hydrated oxide of cadmium on solutions of the ammoniacal salts, the author obtained results different to those announced by Tassilly (*Ann. Chim. Phys.*, [7], vol. xvii., p. 107). By the prolonged boiling of a solution of sal-ammoniac with an excess of oxide of cadmium, a liquor was obtained which deposits first of all a mixture of the ammoniacal chloride, $\text{CdCl}_2(\text{NH}_3)_2$, and the double chloride, then a mixture of rhombohedra, $(\text{CdCl}_2, 4\text{NH}_4\text{Cl})$, and of needles, $(\text{CdCl}_2, \text{NH}_4\text{Cl})$, and, finally, large crystals of the double chloride containing $4\text{NH}_4\text{Cl}$. These latter crystals are decomposed by water, as announced by Rünbach (*Berichte*, vol. xxx., p. 3073), giving 3 molecules of NH_4Cl , and the chloride $\text{CdCl}_2, \text{NH}_4\text{Cl}$. With bromide of cadmium, under the same conditions as above, the author obtained the ammoniacal bromide, $\text{CdBr}_2(\text{NH}_3)_2$, and then bromide of ammonium. By leaving the solution over sulphuric acid, monoclinic crystals of $\text{CdBr}_2, 4\text{NH}_4\text{Br}$ can be obtained; these are decomposed by water like the corresponding chlorised compounds. The mother-liquors still contain the monobromide, $\text{CdBr}_2, \text{NH}_4\text{Br}, \frac{1}{2}\text{H}_2\text{O}$, which is not decomposed by water. This salt, which is always contaminated with the salt containing $4\text{NH}_4\text{Br}$, is, however, easily prepared from its constituents. The action of cadmium hydrate on iodide of ammonium in the same manner gives the compounds, $\text{CdI}_2(\text{NH}_3)_2$ and $\text{CdI}_2, \text{NH}_4\text{I}, \text{H}_2\text{O}$.—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 49.

THE ULTRA-VIOLET SPECTRUM OF RADIUM.*

By Sir WILLIAM CROOKES, F.R.S.

THE spectrum of radium has been examined and the wave-lengths of many of its lines given by several observers, amongst whom I may include Exner and Haschek,† Berndt,‡ Damarçay,§ and Runge.||

Between these observers, however, there are great discrepancies, lines given by one being absent in other lists, and the wave-lengths even of strong lines varying between wide limits. Being in possession of perhaps the purest radium hitherto employed for spectrum work, I have used some of it in photographing its ultra-violet spectrum. The negatives so obtained have enabled me to get measurements from which the wave-lengths of the lines have been calculated with an accuracy only limited by the accuracy of the iron lines used as standards.

The spectrograph itself is a five-prism quartz instrument which I have had in use since 1894. A general idea can be gained of the arrangement of the spectrograph from the accompanying outline plan (Fig. 1). The light from the source *a*, passes first through the condenser, *b*, on to a slit, *c*, thence to the collimating lens, *d*, and round the train of prisms, *e*. It then passes through the camera lens, *f*, whence it falls on the sensitive film in the holder,

luminous centre, and if the spark is close to the slit we have to contend with other irregularities; the image is not clear, and the lines are often confused and blurred. If the spark is moved away from the slit the spectrum gains in definition; the greater the distance between the light and the slit the finer is the sharpness and definition of the lines, but at the same time the loss of light is great. This loss of light, however, may be obviated in great measure with considerable improvement of the definition by inserting optical condensers between the spark and the slit. I use two condensers of quartz, plano-cylindrical, one being double the focus of the other, the axes intersecting each other at an angle of 90°; the object being to concentrate a line instead of a point of light on the slit. All optical condensers waste much light. I use them more to obtain well-defined images than to abridge the time of exposure.

The slit is made of two shallow-angled quartz prisms, as I have already described (CHEMICAL NEWS, vol. lxxi., p. 175, April 11, 1895; *Roy. Soc. Proc.*, vol. lxx., p. 241), and the distance apart of the jaws is generally 0.01 m.m.

The quartz prisms, of which there are five, are of 60°, made in two halves of 30° each, according to Cornu's plan, one half being right-handed and the other half left-handed. The contact surface of both bisects the refractive angle of the entire prism, and is placed perpendicularly to the

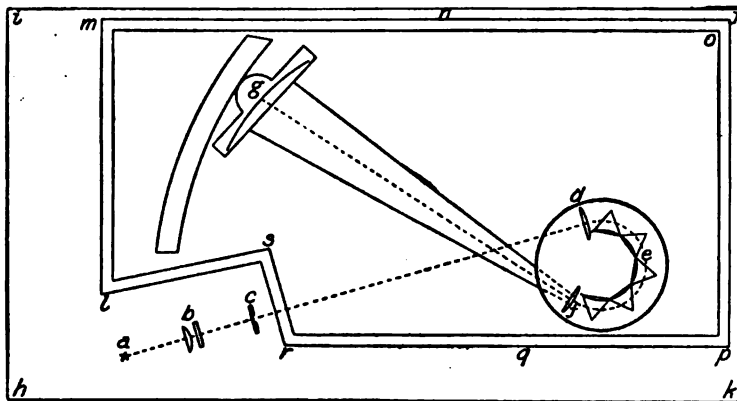


FIG. 1.

g. The whole apparatus is mounted on a planed cast-iron table, *h, i, j, k*, 49½ inches long, 31 inches wide, and 1½ inches thick. The prisms, lenses, and photographic film-holder are enclosed in a large wooden framework, *l, m, n, o, p, q, r, s*, having aluminium shutters on each side, so that the inner adjustments can be effected easily. The height of the enclosure is 28 inches, and the whole is perfectly light-tight when the shutters are down. Outside the dark enclosure, in the space *h, i, s, r*, are situated the arrangements for producing the light to be examined, the optical condensers, and the slit.

An electrical condenser of 180 square inches is intercalated in the secondary circuit, and a coil of twelve turns of well-insulated wire, each turn being 12 inches in diameter, is interposed in the path of the secondary current. This introduction of self-induction in the circuit suppresses most of the air lines, and gives the metal lines on a black background.

The optical efficiency of a spectrograph depends in no small degree on the way in which the source of light is presented to the slit. If the electrodes are too far apart there is distortion, owing to each pole forming its own

crystalline axis of both prisms. In this way duplication of lines is avoided.

The sensitive film-holder must be set at an angle varying with the portion of the spectrum being photographed, as the focus of the less refrangible is longer than that of the more refrangible rays. Moreover, the focal plane is not flat, so the film itself must follow the diacaustic curve, or the lines on it will not all be in focus together (CHEM. NEWS, vol. lxxii., p. 87, August 1895; and vol. lxxiv., p. 259, November, 1896; *Proc. Roy. Soc.*, vol. lxx., p. 242). For this reason glass plates cannot be used, and celluloid films are employed.

To obtain the best definition of any desired line for measurement, expose for a long time and develop briefly, using plenty of potassium bromide in the pyro developer. It is impossible to photograph properly the whole spectrum with a single exposure, so as to have it well defined in all parts, since the brightest lines are over exposed and blurred sideways before the faint ones are impressed. This important fact is too generally lost sight of in spectrum photography.

For correct determination of wave-lengths, it is necessary to photograph on the same film the spectrum of a metal whose lines are known. I generally use iron for this purpose; it has the advantage of giving a large number of very fine lines, the wave-lengths of which have been accurately measured, and not being very volatile the poles do not rapidly wear away. By means of diaphragms

* A Paper presented to the Royal Society, August 1, 1903.

† Franz Exner and E. Haschek, *Wien Akad. Sitzber.*, vol. cx., July 1901; CHEM. NEWS, vol. lxxvi., p. 247.

‡ G. Berndt, *Physikalische Zeitschrift*, 2 Jahrg., No. 12; CHEM. NEWS, vol. lxxviii., p. 77.

§ Damarçay, *Comptes Rendus*, vol. cxxix., p. 716; vol. cxxxi., p. 258.

|| C. Runge, *Astrophysical Journal*, vol. xli., p. 1.

WAVE-LENGTHS OF THE RADIIUM LINES ACCORDING TO DIFFERENT AUTHORITIES.

Runge.	Demarçay.	Exner and Haschek.	W. Crookes.	Intensity.	Remarks.
		2512·46			I cannot see this line on my photographs.
		2736·2	2709·06	20	This is close to an iron line, 2709·14.
		2813·60	2813·876	30	I cannot see this line on my photographs.
		2816·25			Comes between a fine pair of platinum lines.
		2831·98			Probably a platinum line, 2816·1.
		2877·10			I cannot see this line on my photographs.
		2908·0			Probably an iridium line, 2877·1.
		2976·17			Probably a platinum line, 2908·1.
		3079·97			Probably a platinum line, 2975·9.
		3126·53			Probably a platinum line, 3079·8.
		3541·77			I cannot see this line on my photographs.
3649·77	3649·6	3649·33	3649·712	70	Ditto.
			3809·393	10	A very strong radium line.
			3812·170	5	A faint radium line.
3814·591	3814·7	3814·62	3814·661	100	A faint radium line.
		3861·77			The strongest line in the radium spectrum.
			3961·627	5	I cannot see this line on my photographs. Exner and Haschek include it in their radium lines, but in a note say it is not a line of radium.
		3993·25			A faint radium line.
			4010·397	10	Probably a barium line, 3993·69.
		4053·81	4053·124	10	A faint radium line.
4341·0	4340·6		4340·619	5	A faint radium line.
	4364·2				I cannot see this line on my photographs.
4436·45	4436·1				Probably a platinum line, 4437·5.
	4458·0				Demarçay says this is the centre of a nebulous band, which begins at 4463·7, has a maximum from 4453·4 to 4455·2, and ends at 4390·0. I cannot see this on my photographs.
4533·33	4533·5				I cannot see this line on my photographs.
	4600·3				Demarçay says (with a query) that this line does not belong to radium.
	4627·4				I cannot see it on my photographs.
					Demarçay says this is the centre of a nebulous line, which begins sharply at 4621·9, has a maximum at 4627·5, and ends about 4631. I cannot see it on my photographs.
4682·346	4641·9	4682·41	4682·149	25	I cannot see this line on my photographs.
	4683·0				A strong radium line.
	4692·1				I cannot see this line on my photographs.
	4699·8				Ditto.
	4726·9				Ditto.
		4781·4			Ditto.
4826·14	4826·3		4825·896	15	A strong radium line.
5813·9			5813·9		This is a strong citron line, outside the range of my photographs.

close to the slit the experimental and the standard spectra are photographed on the same film, overlapping for about 1 m.m. in the centre (*Roy. Soc. Proc.*, vol. lxx., p. 243). The photographs are then transferred to a measuring machine, and from the figures thus obtained the wave-lengths are calculated.

The radium was used in the form of nitrate, a well-crystallised salt easily soluble in water. The induction spark was taken between platinum poles partly immersed in a strong solution of the salt. On this account the nitrate was used in preference to the chloride. Much platinum is always dissolved when the poles are sparked in a solution of a chloride, while with nitrates this does not occur to the same extent.

The solution was strong, and slightly acid with nitric acid. Many forms of spark tube were tried before a satisfactory form (shown in Fig. 2) was devised. A B is a tube of hard Jena glass with a bulb at the lower end. At the bottom of the bulb a platinum wire is sealed in, and in the upper part of the tube, at B, a short piece of tube is ground in to form a stopper. A long platinum wire passes through from this stopper, bare at the upper part, and guarded with glass inside the bulb tube. A hole, c c, is made at one side of the bulb to form a window, and a piece of platinum tube is put round the lower platinum wire at D, so that its upper end is about 3 m.m. above the end of the wire it surrounds, and a millimetre below the centre of the window, c c. The upper wire should be about 1 m.m. from the top of the

platinum tube surrounding the lower wire. Any solution put in the lower part of the bulb is sucked up by capillarity to the top of the platinum tube, and an induction spark between the two wires gives a spectrum of any metal in solution. When exposures of more than ten minutes or so are required, it is necessary to introduce fresh solution to keep the level in the bulb constant. This is easily done during the exposure by means of a small pipette. The splash of the spark throws drops of liquid for some distance, and the heat and decomposition cause nitric acid to come off. These are objectionable when falling on delicate apparatus, and they cause great waste of solution, which with rare bodies is to be avoided; to prevent this a branch tube is sealed in near the top of the spark tube, dipping to the bottom of a flask through a cork. Another tube passes just through the cork, and is connected with an aspirator. During the sparking operation a rapid current of air is drawn in through the window, and all splashes and vapours are washed through the water in the wash-bottle. Thus the acid fumes are kept from injuring the apparatus, and the valuable salt is saved in the wash water.

The presence of platinum lines is due to the platinum poles between which the spark is taken. They are easily identified by photographing a platinum spectrum and a platinum-radium spectrum on the same plate, slightly overlapping one another. The platinum being common to both, gives continuous lines across the two spectra, while the radium lines only appear in one spectrum. Radium

being purified from barium by a tedious process of fractional crystallisation of the bromides is almost certain to show barium lines in its spectrum. I have only been able to use about a grain of perfectly pure radium bromide, all other samples containing traces of barium.

Owing to the length of the spectrum and the necessity of having the lines near the position of minimum deviation to get the greatest sharpness, each photograph is limited to a small extent of spectrum, and eight exposures are needed to take in the whole ultra-violet spectrum, and as far into the visible part as the plates are sensitive to.

The accompanying table gives the wave-lengths of all the lines ascribed to radium by different observers. Many of the early observations are necessarily imperfect, owing to the enormous difficulty of preparing radium compounds of sufficient strength to show a photographed spectrum. And when sufficient concentration was obtainable, the observations were necessarily limited owing to the minute amount available rendering verification difficult.

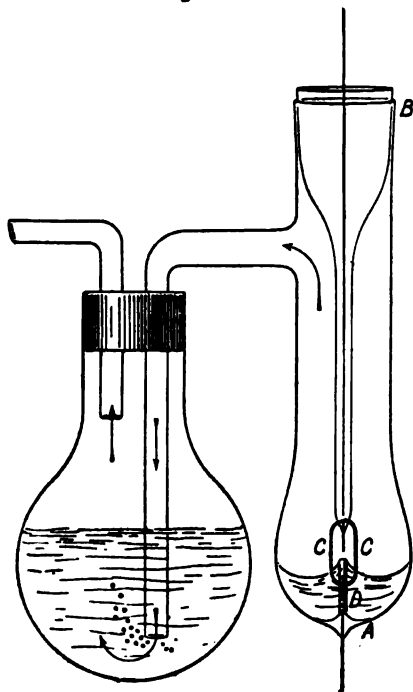


FIG. 2.

Measurements are taken of the exact distances apart of the radium lines and certain adjacent iron lines used as standards. By using a formula, first communicated to the British Association by Sir George Stokes, the wave-lengths of the unknown lines can be calculated. At the time the formula was given it was sufficiently accurate for the instrumental means employed for photographing spectra, but the formula only gave approximate results, and the accuracy of determination of wave-lengths has since improved so much that a correction is required to the original formula. Sir George Stokes, before whom I placed the difficulty in June, 1895, quickly solved it in a satisfactory manner. The usual formula requires the positions of two standard lines of known wave-lengths, n_1 and n_3 , on each side of the unknown line, n_2 . To make the small correction, Sir George advised me to take a third line of known wave-length, chosen well removed from the selected known lines n_1 and n_3 . If chosen in the interval 1-3 it had better not be greatly distant from the middle. There is, however, very wide latitude of choice in this respect. All these lines must be photographed and measured in the usual way. Calculate the approximate wave-length of the

unknown line by the original formula, and then calculate the approximate wave-length of the third known line by the same formula, as if it were unknown, using the two original standards for this purpose also. We have now the approximate wave-length of a known line, as given by the formula, and also its true wave-length. The difference between these two values leads (see below) to the correction to apply to the approximate value of the unknown line.

It often happens that four or more lines are well placed for use as standards. If any three of these be taken, and from them the positions of the other lines be calculated, it will sometimes be found that there is a small residual error in some of them. In such a case the error can be minimised by adjusting the value of the three primary standards so that the sum of the errors on all the lines is a minimum, and in no individual case is very great. Then, with these three corrected standards, the unknown lines may be calculated with confidence to seven figures.

With few exceptions my standards are the most recent published by Rowland. He has given two sets of "Standard Wave-lengths," one in "Astronomy and Astrophysics," vol. xii., p. 321, published in 1893; the other in the *Astro-physical Journal*, vol. i., No. 1, January, 1895, to vol. v., No. 3, March, 1897, and vol. vi., No. 5, December, 1897. Any systematic or accidental error found to occur in Rowland's figures will require a corresponding correction of my own wave-lengths. Assuming Rowland's wave-lengths to be correct, I can follow his seven-figure standards with a probable error of ± 0.002 at the most refrangible end, and one of ± 0.01 at the least refrangible end. The average error being ± 0.005 . But on the assumption that all Rowland's measurements are incorrect by a variable amount, as rendered probable by the recent work of Fabry and Perot (*Comptes Rendus*, May 28, 1901, vol. cxxxii., No. 21), a correction will have to be made which will affect the sixth figure.*

For the reduction of the lines 4682.149 and 4825.896, there being no well-defined iron lines suitable for measurement, I have used some strong zinc and cadmium lines, which also have been measured by Rowland.

The following is the method of calculation I now employ:—

$$\begin{array}{ll} n_1 & \lambda_1 \\ n_2 & \lambda_2 \\ n_3 & \lambda_3 \\ n_4 & \lambda_4 \end{array}$$

n_1 and n_3 are scale positions on the measuring machine of standard lines of known wave-lengths, λ_1 and λ_3 . n_2 is the scale position of the line whose wave-length is required (λ_2).

n_4 is the scale position of an additional standard line whose wave-length is known. It is used for obtaining the correction to apply to the approximate wave-length of λ_2 .

E_2 and E_4 are the calculated errors obtained for λ_2 and λ_4 , which have to be added to or subtracted from λ_2 or λ_4 to get them accurate.

For the tedious calculations involved in the reduction of the wave-lengths I am indebted to my son, Mr. Bernard H. Crookes, M.Sc.

Rule.

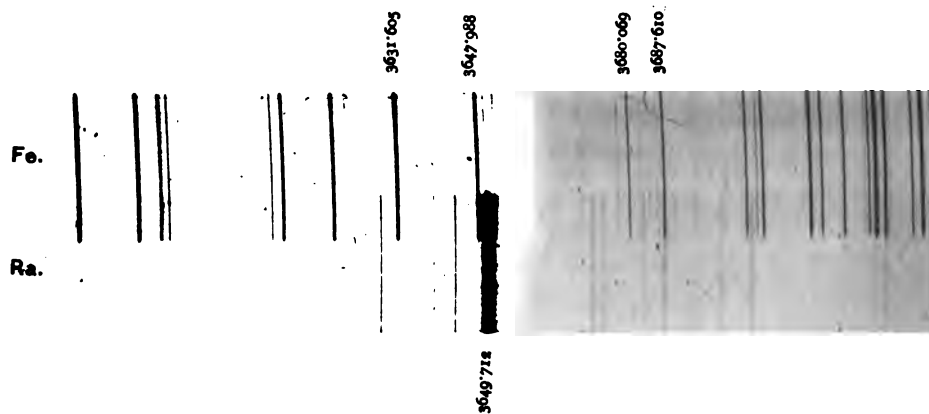
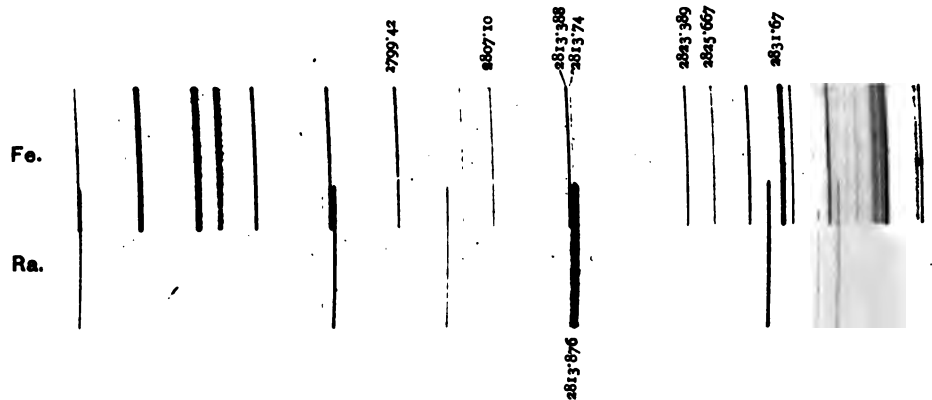
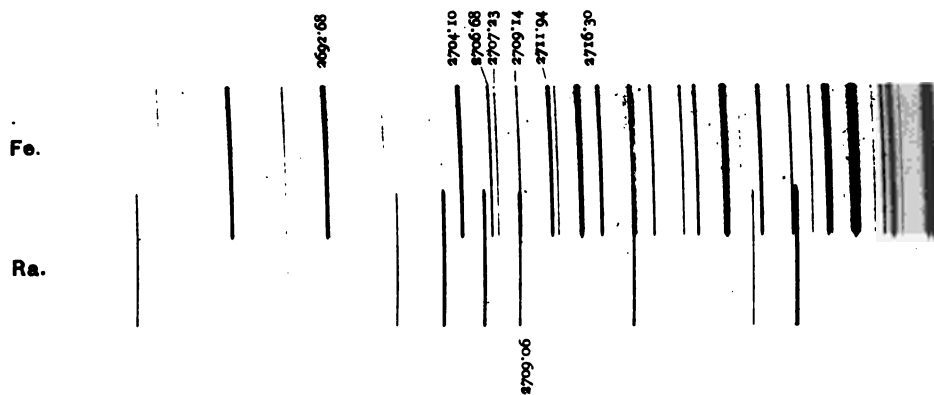
First calculate the approximate value of λ_2 by the following formula:—

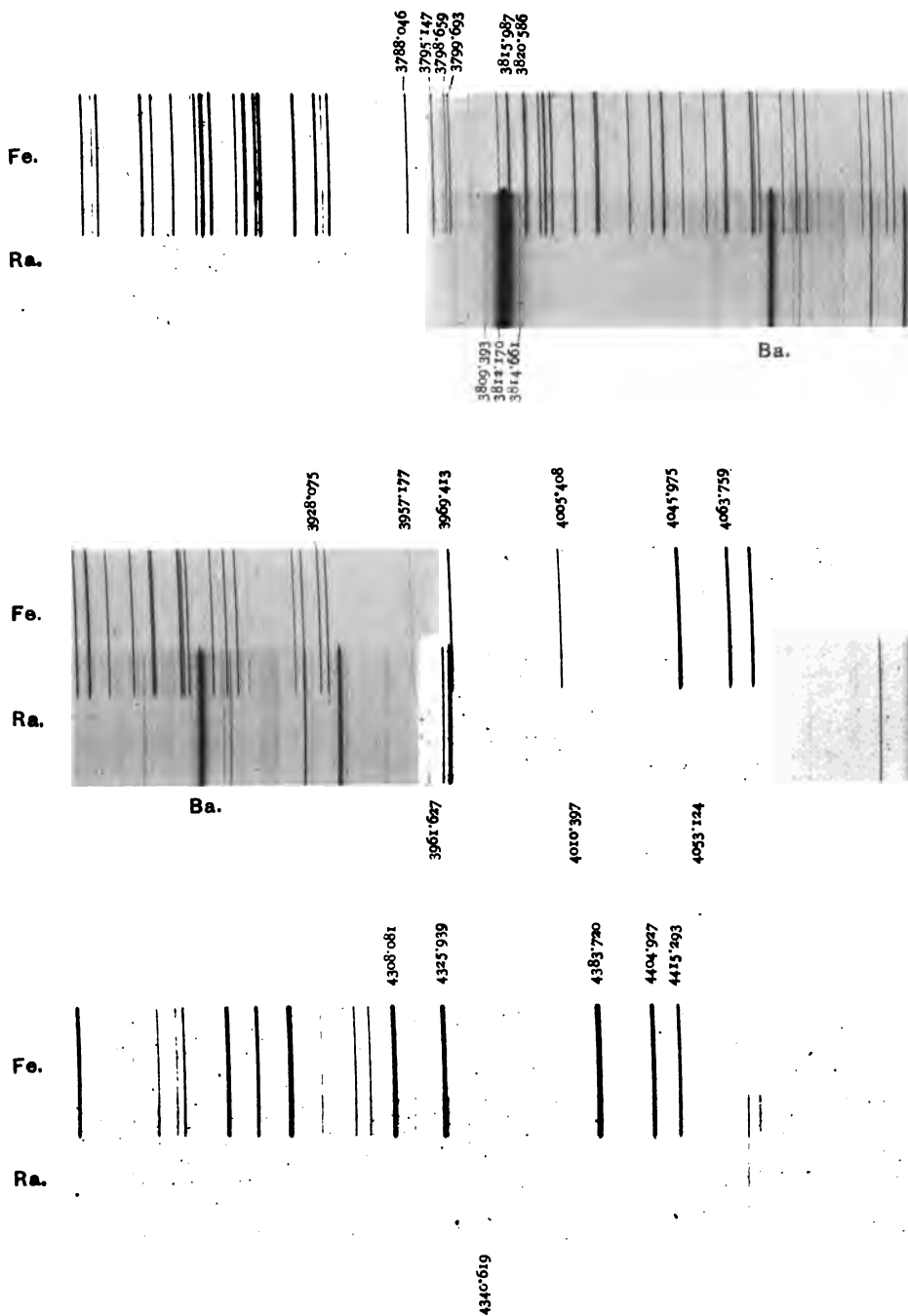
$$\frac{\lambda_3^2 \lambda_1^2 (n_3 - n_1)}{\lambda_1^2 (n_3 - n_1) + \lambda_3^2 (n_3 - n_2)} = \lambda_2^* \text{ (approx.)} \quad (1)$$

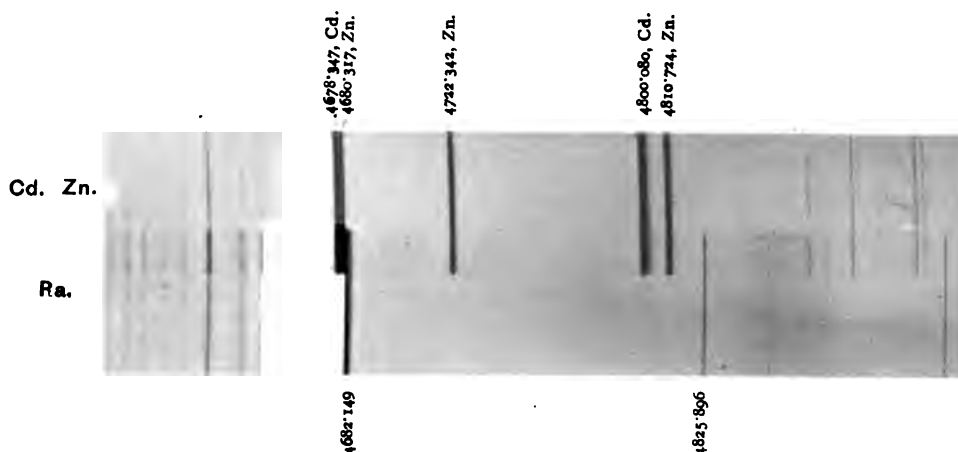
Next, in a similar way, find the approximate value of λ_4 , using the following formulæ:—

$$\frac{\lambda_3^2 \lambda_1^2 (n_3 - n_1)}{\lambda_1^2 (n_3 - n_1) + \lambda_3^2 (n_3 - n_4)} = \lambda_4^* \text{ (approx.)} \quad (2)$$

* Measuring a ruled glass micrometer in my measuring machine I find the average of ten scale readings can be relied on as not more than 0.0002 inch in absolute error on an average, with occasional errors of double this amount, and of course many errors of less, or zero. The effect of an error of this magnitude represents an error of 0.0025 in the wave-length at one end of the spectrum, and one of 0.011 at the other end.







THE ULTRA-VIOLET SPECTRUM OF RADIUM.

The Collotype illustrations are from the original negatives, and are entirely untouched. The grain of the process somewhat diminishes the sharpness of the lines.

To economise space and avoid unnecessary complications, I have given photographs of only that part of the spectrum adjacent to the radium lines. Had the whole spectrum been given as photographed, the length would have extended to more than 10 feet.

The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower halves contain the radium lines, with their wave-lengths as calculated from the iron standards. The other lines on the lower halves are chiefly platinum lines. On the 4th and 5th photograph a strong barium line is shown at wave-length 3891.97 (Rowland), or 3892.42 (Exner and Haschek).

In the part of the spectrum shown on the last strip there are no iron lines suitable for standards. Here, therefore, I have used some good lines of zinc and cadmium the wave-lengths of which are given in Rowland's latest table.

Then—

$$\lambda_4 \text{ (true)} = \lambda_4 \text{ (approx.)} \pm E_4.$$

Now calculate E_2 by the following equation:—

$$\frac{(\text{Approx.}) \lambda_1^2 (n_2 - n_1) (n_3 - n_1)}{(\text{Approx.}) \lambda_4^2 (n_2 - n_1) (n_3 - n_1)} E_4 = E_2 \quad (3).$$

Then—

$$(\text{Approx.}) \lambda_2 \pm E_2 = \lambda_2.$$

[In fact, writing y for λ^{-2} , of which the refractive index is a function, and x for n , the graph of the relation between y and x may in this neighbourhood be identified with a parabola. The formulæ (1) and (2) neglect the effect of its curvature, by taking the points 2 and 4 to be on the chord connecting the points 1 and 3. The corrections E_2 and E_4 are thus connected with the distances from the points on this chord to the true points on the curve by the formula $\delta y = -2E/\lambda^3$; and the formula (3) connecting them is the expression of a well-known geometrical property of a parabola].

Example.

Calculate a radium line from adjacent iron lines as standards.

$$n_1 = 0.000000. \quad \lambda_1 = 2813.388 \text{ (Rowland).}$$

$$n_2 = 0.005310. \quad \lambda_2 = \text{A radium line.}$$

$$n_4 = 0.107143. \quad \lambda_4 = 2823.389 \text{ (Rowland).}$$

$$n_3 = 0.131020. \quad \lambda_3 = 2825.667 \text{ (Rowland).}$$

$$\begin{array}{rcl} 2 \log \lambda_1 & 6.8984593 & 2 \log \lambda_3 \quad 6.9022420 \\ \log 0.00531 & 3.7250945 & \log 0.125710 \quad 1.0993698 \\ \log 42029.46 & 4.6235538 & \log 1003718.32 \quad 6.0016118 \\ & & 42029.46 \end{array}$$

$$\log 1045747.78 = 6.0194269$$

$$\begin{array}{rcl} 2 \log \lambda_3 & 6.9022420 & \\ 2 \log \lambda_1 & 6.8984593 & \\ \log 0.131020 & 1.1173776 & \end{array}$$

$$\begin{array}{rcl} \log \text{numerator} & 12.9180389 & \\ \log \text{denominator} & 6.0194269 & \end{array}$$

$$2) \quad 6.8986120$$

$$3.4493060 = \log 2813.883 = \lambda_2 \text{ (approx.)}$$

$$\begin{array}{rcl} 2 \log \lambda_1 & 6.8984593 & 2 \log \lambda_3 \quad 6.9022420 \\ \log 0.107143 & 1.0299638 & \log 0.023877 \quad 2.3779798 \\ \log 848053.20 & 5.9284231 & \log 190643.44 \quad 5.2802218 \\ & & 848053.20 \end{array}$$

$$\log 1038696.64 = 6.0164887$$

$$\begin{array}{rcl} \log \text{numerator} & 12.9180389 & \\ \log \text{denominator} & 6.0164887 & \end{array}$$

$$2) \quad 6.9015502$$

$$3.4507751 \log 2823.418 = (\text{approx.}) \lambda_4$$

$$\begin{array}{l} \text{But—} \quad \lambda_4 = 2823.389 \\ \therefore \quad E_4 = 0.029 \end{array}$$

$$\begin{array}{rcl} 3 \log \lambda_2 & 10.3479 & 3 \log \lambda_4 \quad 10.3523 \\ \log 0.005310 & 3.7251 & \log 107143 \quad 1.0300 \\ \log 0.12571 & 1.0994 & \log 0.023877 \quad 2.3780 \\ \log \text{numerator} & 7.1724 & 7.7603 \\ \log \text{denominator} & 9.2979 & \log 0.029 \quad 2.4624 \\ & 3.8745 & 9.2979 \end{array}$$

$$\begin{array}{l} \therefore E_2 = 0.007 \\ \lambda_2 = 2813.876 \end{array}$$

EXPERIMENTS AND OBSERVATIONS WITH RADIUM COMPOUNDS.*

By WILLIAM ACKROYD, F.I.C., F.C.S.

THE telluric distribution of radium is 0.0003 when gold = 1 (B. A. Report, 1902, p. 581; CHEMICAL NEWS, lxxvi., 187). It has therefore the claim to be regarded as the rarest element known at present. The effects produced by rays from its compounds simulate those of heat to a certain degree, as will be seen in the following account of my experiments and observations, which include some results of a negative character because of their probable bearing on the problem of the origin of the energy of these compounds.

Phosphorescence.

Attention was early turned to observations with diathermanous common salt, NaCl, under the influence of radium rays. Sealed glass tubes containing 5 m.grms. of the pure radium bromide were used, unless otherwise stated. Such a tube resting in common salt produced marked phosphorescence, which lasted for hours after the removal of the exciting cause (Ackroyd, *Nature*, July 23, 1903). A two minutes action of the phosphorescing salt on a photographic plate resting over but not in contact with it, was apparent on development. Slides of the photographic effects are shown of:—(1) A radium bromide tube, with two minutes exposure. (2) The radium bromide tube plus the sodium chloride in which it was imbedded; two minutes exposure. (3) Sodium chloride alone after excitation for some hours with radium bromide; thirty minutes exposure. On the first slide is also shown the photographic action of a tube of radiferous barium chloride, to which reference is made later; its radio-activity compares favourably with that of the 5 m.grms. of pure radium bromide.

The table-salt experimented with was of slightly alkaline reaction to red litmus-paper, and contained traces of the usual impurities. The compound was therefore prepared (1) by precipitation with hydrochloric acid from its solution in distilled water, filtering, drying, and igniting; and (2) by the neutralisation of caustic soda with hydrochloric acid. In each case the sodium chloride obtained became phosphorescent under the radium bromide rays. Sodium chloride, with a trace of moisture in it, gave better results than the compound kept carefully dry in a desiccator after ignition; the difference in this respect was very striking on comparison of the phosphorescence of ignited and unignited salt two hours after removal of the radium bromide tubes. The sodium chloride also exhibited phosphorescence when moistened with hydrochloric acid a little over normal strength. The simulation of heat effects becomes apparent on comparing these results with hitherto recorded observations. Sir David Brewster observed phosphorescence when solution of common salt was poured into a cup of heated iron (Blackie's "Pop. Ency.," xi., 49), and Phipson records that common salt is phosphorescent only at a temperature of about 200° C. ("Phosphorescence," p. 20).

Lithium chloride prepared from the carbonate and then fused and ground up into a fine powder exhibited phosphorescence; when, however, the moisture present (absorbed from the atmosphere in twenty-four hours) became excessive, it ceased to phosphoresce in radium bromide rays.

Potassium chloride phosphoresced under the influence of the rays, but there appeared to be no notable phosphorescence on their removal. The after-phosphorescence of potassium bromide was plainly visible; negative results were obtained with sodium and potassium iodides. It is interesting to note that in the phosphorescence of the halides of the metals of the alkalis induced by radium rays there is *decrease* with increase of atomic weight; whereas, with metals of the alkaline earths insoluble in effective radiant energy produces an *increase* with increase of atomic weight. These remarks are based on a comparison of the

* A Paper presented to the British Association (Section B), Southport Meeting, 1903.

extreme members of each series, so far as they have been experimented with, and take no account of possible variations in the intermediate members.

The phosphorescence observations were made in a dark room after the eyes had adapted themselves in every case to the absence of light and had attained the necessary degree of sensitiveness to very faint lights.

Colour Change.

Sodium chloride is changed in a few hours from white to orange or buff colour; the freshly ignited salt appeared somewhat pinker in tint. Moistening with hydrochloric acid did not appear to interfere with the change. No colour change was observed with lithium chloride. The absence of change in the lithium salt, the change in the sodium compound, and the order of change in the latter case are all colour facts of somewhat the same character as those I have grouped under the term metachromatism,* where inorganic bodies are changed in colour in the order of the meta-chromatic scale under the influence of sensible heat, and where the tendency to change is least evident in the lightest members of a comparable group. There is the difference, among others, however, that here the changes are more isomeric in their nature, as they appear to last for some time in dry compounds. On the other hand, there may be rapid reversion to the original colour in moist compounds. Thus in potassium chloride made by neutralising caustic potash with hydrochloric acid, crystallising, and then draining, we get crystals of an acid reaction which readily turn from white to violet under radium bromide rays, and on removal of the radium bromide regain the white colour in less than a minute. A similar reversion was observed in moist acid sodium chloride, whereas the dry compound took many days to regain its original whiteness when exposed to daylight. Where change is effected by radium rays the colours produced remind one forcibly of the colours of flowers and of De Candolle's division of them, for they divide themselves into xanthic and cyanic series. The only member of the blue or cyanic series so far discovered is the one which has been variously termed violet, purple, or amethyst. Here there is a striking difference between these phenomena and those of metachromatism. In the latter, all known white compounds which change colour do so to yellow or the xanthic series only; with the changes of white bodies effected by radium rays the new colour may belong to either class.

Bicarbonate of soda is changed to amethyst colour in twenty-four hours, and the same change is exhibited by meta-bisulphite of potash. The Curies discovered that soda-glass is changed from colourless to violet, a change which Becquerel further observed is accelerated by a temperature of 100° C. The French observers have attributed the alteration to the presence of manganese. In this connection it is of interest to note that the violet colour of the amethyst has also been usually attributed to the presence of a small percentage of an oxide of manganese; a reason has been assigned in which this compound plays no part (*vide* Watts's "Dict. of Chem.," v., 1). It appears to me not improbable that in these cases we have physical colour changes of the same kind as that of the bicarbonate of soda, a view which is strengthened by the chemical analogies existing between the compounds of carbon and silicon as contiguous members of the same periodic group, and by the extreme ease and quickness with which the violet glass is made to revert to its original colourless condition at a high temperature.

The various colour changes mentioned in this section were effected in the dark room by imbedding the radium bromide tube in the compound experimented with.

Other Heat Relations.

The Curie demonstration of the evolution of heat by

radium compounds has been effected by bringing the substance into surroundings of lower temperature. I have attempted to reverse the conditions. A radium bromide tube was enclosed in a paper cylinder which had been painted with one of Meusel's sensitive colour-changing compounds, preferably the yellow Ag_2HgI_4 . It was argued that in a medium of gradually rising temperature the heat from the radium compound within, plus the heat from without, would cause the transition colour change of the paper to be observed earlier in those parts in contact with the radium salt than in those not in contact. The paper cylinder and its enclosed tube were put inside a dry test-tube, which was introduced into a beaker of warm water at or near the transition temperature of the mercury salt; the temperature of the water in the beaker was slowly and gradually raised; the effect looked for was not obtained. Among the reasons that may be given for this negative result is the one that the radium compound was drawing its energy from an external source during the gradual rise of temperature, and therefore behaved no differently from a blank. This is in keeping with Becquerel's observation of the accelerating influence of a rise of temperature on the colour-changing power of rays from a radium compound acting on its glass envelope.

In further repetition of this experiment an endeavour was made to eliminate the glass by emptying a quantity of radiferous barium chloride direct into one of the coloured paper cylinders. The same negative result was obtained. Here the fact was discovered incidentally that the mixture of radium and barium chlorides in such a moist atmosphere lost its power of phosphorescing and of inducing phosphorescence in barium platinocyanide. Numerous attempts to revivify it by chemical means failed, and only ignition in a platinum crucible restored its original qualities (compare F. W. Branson, *Nature*, July 30, 1903). This fact destroys the contention that nothing can be done to a radium compound to diminish or destroy its radio-activity, and it appeared of such importance that it has been several times repeated. In one of these experiments freshly ignited radiferous barium chloride was divided between two tubes and sealed off; both exhibited the quality of continuous phosphorescence in a dark room day after day. The end of one was now drawn out, and water admitted by the capillary thread. With the introduction of moisture the phosphorescence practically ceased. No such result was obtained with a tube of pure radium bromide similarly treated as the phosphorescence after the introduction of distilled water was apparently undiminished. The explanation I advance in the former case is that the water and barium chloride absorb the obscure radiant energy coming from surrounding bodies, which otherwise would have been communicated to the radium compound to make it phosphoresce. It may be mentioned here that moist barium chloride alone gave negative results in radium bromide rays, or, in other words, it is a non-phosphorescent substance.

The following is now suggested as the explanation of one of the causes of the continuous phosphorescence of radium compounds. The salts of the metals of the alkaline earths are notably phosphorescent under the influence of suitable exciting rays, and the phosphorescence lasts for hours after insolation; compounds of radium, as the end member of the series, possess the property in an increased degree, and their phosphorescence lasts very much longer still. The cause in the latter case—external radiant energy—is a periodically recurring one, and the excited phosphorescence produced by its absorption lasts longer than the interval between two periods of excitation, and therefore appears continuous. Radium compounds are thus energy transformers to an abnormal degree. Only an effective sifter of the external energy which affects them can stop their manifestations. Ice and most bodies appear to be more or less transparent to this form of radiant energy; the most effective sifters remain to be discovered, and will probably consist for the most part of non-phosphorescent halides.

* CHEMICAL NEWS, vol. xxxiv., p. 75.

THE THEORY OF DYEING.*

By G. von GEORGIEVICS.

THE author gives a brief historical introduction to the subject of tinctorial chemistry, and observes that the study of this branch of applied science has been greatly complicated by the publication of large masses of incompletely observed facts. He further remarks that practical unanimity prevails as to the nature of the dyeing process in so far as concerns the application of colours such as chrome yellow, nitraniline red, and the mordant colours; these colours, or compounds of the colours with the mordant, are deposited as such upon the fibre.

The theories, or more properly the hypotheses, concerning the nature of dyeing refer more particularly to the so-called substantive colours; that is, to dyeing with acid colours, basic colours, and direct colours. The principal theories of the process of dyeing are two in number; namely, (1) the chemical theory, and (2) the mechanical theory. In accordance with the first, the dyeing of wool and silk with acid and basic colours is due to the formation of chemical compounds between the colour and the fibre; the chemical combination is supposed to be of a loose, salt-like nature, because the combined colour exhibits a chemical behaviour identical with that of the free colour. The chemical theory offers no plausible explanation of dyeing with direct cotton colours.

The mechanical theory describes the process of dyeing as one of absorption or of solution. Some writers attempt to compromise by describing the dyeing process as partly chemical and partly mechanical in nature, whilst others are of the opinion that the dyeing changes in character with the dye-stuff and the fibre.

In discussing what is required of a theory of dyeing the author states the view that such a theory can be nothing more nor less than an expression of all the hitherto known facts concerning the process. The supporters of the mechanical theory of dyeing do not deny the possibility of the existence of chemical combination, more especially as all colours are of acid or of basic nature, and the animal textile fibres, at least, are not chemically indifferent; they claim, however, that the existence of such a chemical combination has not been hitherto proved in any single case, whilst all the observed facts tell in favour of the mechanical theory. The supporters of the chemical theory of dyeing put forward, as specially important pieces of experimental evidence, two statements, both made by E. Knecht, the one referring to the dyeing of basic colours on wool and silk, the other to dyeing with acid colours. In accordance with the first statement, wool and silk play the part of acids towards basic colours, and the corresponding coloured compounds must be regarded as salts of the colour with keratin or fibroin respectively, because in such dyeing processes the acid is quantitatively split off from the colouring matter, and only the colour base is taken up by the fibre. It is further suggested that the colourless rosaniline base can only give rise to the fuchsin red colour by formation of a salt.

Since this time, however, the author has shown that in dyeing chemically indifferent substances, such as glass and china-clay, which cannot play the part of acids, the acid of the basic colour remains quantitatively in the dye-bath; he has further shown that the rosaniline base exists in a coloured form. The full force of this contradiction of the chemical theory is not fully admitted, it having been objected that many kinds of glass are slightly attacked by water and are thus not chemically indifferent. The author showed many years ago, however, that this objection is founded upon a total disregard of the fact that the results are of a quantitative nature. The author remarks that whilst the attack has been directed against the strong part of his work, its weak point—which is as follows—has not hitherto been noticed. The fact that in the

dyeing of chemically indifferent substances with basic colours the acid part of the latter remains quantitatively in the bath is only a proof that one has to deal with the same phenomenon which is observed in the dyeing of silk and wool, and is not an indication that salt formation has taken place between the colour base and the fibre substance; the dyeing of glass and china-clay is, at any rate, a process of absorption, and its external similarity with the dyeing of silk and wool with the same colours is not necessarily a proof of the identity of the two processes. The author's work was directed solely against the validity ascribed to the argument repeatedly brought forward in support of the chemical theory, and still leaves open the question of the nature of the process concerned in the dyeing of animal fibres with basic colours. Should it ever be possible to prove the existence of chemical compounds between colour and fibre it will be most probably done in the case just referred to, but such information could certainly not be obtained in the manner only lately attempted by Knecht. Knecht boiled out with alcohol wool and silk dyed with night-blue, and believed himself forced to the conclusion that the extract contained chemical compounds of the night-blue base with keratin or fibroin respectively. If the conclusion were correct, it would be possible by prolonged repetitions of the operations of dyeing and extraction with alcohol to bring about a gradual destruction of the fibre. The improbability of this is obvious, and the author clearly proves the incorrectness of Knecht's final conclusions by a repetition of the work upon which they are based. After precipitating the colour base and eliminating the alcohol, Knecht prepared aqueous solutions from the above mentioned alcoholic extracts, which, according to his statement, possessed the property of precipitating magenta and night-blue, and which he therefore supposes to contain keratin or fibroin respectively, or chemical compounds formed from these two substances during the process of dyeing. On repeating these experiments the author finds that the solutions, if perfectly pure fibre material purified with alcohol has been used, precipitate solutions of magenta only, and that but very slightly indeed. The same precipitate may, however, be obtained if silk and wool are left entirely out of the experiments; he finds that by precipitating the colour base from an alcoholic solution of night-blue with barium hydrate, and by afterwards removing the latter from the solution, a liquid is finally obtained which has the property of precipitating magenta. In this instance it is naturally quite out of the question that keratin or fibroin play any part in the precipitation.

The second principal support upon which the chemical theory rests has also been given by Knecht. It was observed at an early date that molecular proportionality between colour and fibre seems non-existent in dyeing trials; the results thus differ from those obtained in cases of ordinary chemical combination. By dyeing wool in very concentrated solutions of picric acid and similar acid colours, Knecht supposed that he had established the existence of chemical compounds formed in definite molecular proportions. The repetition of these experiments by Perger and Ulrich has, however, shown that Knecht in his desire to make the fibre take up as large a quantity of the colour as possible, used such an excess of colour that part of it was deposited as crystals upon the dyed fibre. It is therefore clear that under such conditions it is absolutely impossible to ascertain, even with a small degree of accuracy, the amount of colour which has been actually taken up by the fibre.

The author considers himself justified in stating that these two fundamental supports upon which the chemical theory of dyeing rests cannot withstand any searching criticism.

A considerable number of facts have accumulated during recent years which tend to strengthen the view that the processes of dyeing are uniform and of a mechanical nature. The author showed in 1894 that, in dyeing silk with indigo-disulphonic acid, the distribution of the colour

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

between the residual solution and silk dyed in it is governed by a law which may be expressed by the formula—

$$\frac{\sqrt{C} \text{ solution}}{C \text{ fibre}} = K;$$

in which C refers to the concentration of the colour solution, and K is a constant independent of the concentration. Later experiments have shown that this law of the distribution of the colour is applicable to dyeing on silk and wool of other acid colours, and also to the dyeing of direct colours (salt colours) on cotton. It is thus proved, first, that the processes of dyeing with the acid colours on the one hand and with the direct cotton colours on the other, are identical in kind, and, secondly, that these processes cannot be of a chemical nature. If a chemical compound were formed, the distribution of the colour between the two media would be of an entirely different character, just as Walker and Appleyard have recently indicated. The author has only lately shown that picric acid and oxyazobenzene are deposited on the fibre in a free state during dyeing with these colours; this seems to be of special importance in the case of picric acid. In view of Knecht's statement, and of the fact that picric acid forms compounds with such great readiness, chemical combination, if at all possible, might have been expected in this instance.

Binz and Schroter have lately endeavoured to show that dyeing with oxyazobenzene differs materially from that of the other acid colours. On account of the fastness exhibited by dyeings with oxyazobenzene these authors assumed that this colour forms a stable compound with the substance of the wool as the result of condensation.

As regards the dyeing of acid colours on animal fibres and that of the direct cotton colours on cotton we may therefore safely say that we possess distinct proof that these processes are identical and of a mechanical nature.

The further questions as to whether substantive dyeings should be considered as solid solutions or as resulting from adhesion is still open for speculation.

A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.*

By HARRISON EASTMAN PATTEN.

(Concluded from p. 196).

Manganous Hydroxide.

Method.—The general method used in this investigation was the same as for chromium and iron. The sulphur trioxide was determined directly in "totals" and "filtrates" after the manganese had been removed. This removal was effected in the following manner:—Sodium acetate solution was added to the "filtrates" and "totals," and the manganese precipitated as MnO_2 by bromine, the excess of bromine boiled off, and the MnO_2 filtered off, well washed, and ignited and weighed as Mn_2O_3 . The filtrate from this MnO_2 was concentrated, and the SO_3 determined as $BaSO_4$. In the case of the "totals," re-solution of the manganous hydroxide was effected with hydrochloric acid just before the sodium acetate was run in. Occasionally the barium sulphate determinations showed a slight colouration, but the quantity of manganese present was of course negligible. I found this method efficient. Re-solution of these complex precipitates of chromium, iron, manganese, zinc, and aluminium, in hydrochloric or nitric acid, has in every case proved sufficient to split them into determinable components.

The chlorine was determined in presence of manganese, a re-solution with nitric acid being first effected, and then

all manganese was washed out of the silver chloride by a wash-water containing 25 c.c. concentrated nitric acid and 0.1 gm. silver nitrate per litre.

Solutions.—A. 98.9 grms. $MnCl_2 \cdot 4H_2O$ was dissolved in water, and made up to 500 c.c. at 20° C. This solution was found to contain the equivalent of 0.05186 gm. MnO per c.c. B. A solution of potassium hydroxide containing 0.02705 gm. KOH per c.c. at 20° C. C. A solution of sulphuric acid containing 0.04046 gm. per c.c. at 20° C.

Experiments I., II., III., IV., V. were made as shown in Table II. Each system contained 50 c.c. manganous chloride, Solution A; 44.24 c.c. sulphuric acid, Solution C, neutralised to potassium sulphate by 75.63 c.c. of potassium hydroxide, Solution B; and varying amounts of potassium hydroxide to cause the precipitation. In every case the potassium sulphate was run into the flask; next the manganous chloride; and, finally, the potassium hydroxide. Then the system was made up to 500 c.c. at 20° C., and well shaken, whereupon four 50 c.c. portions were drawn out with a pipette, and labelled "totals." The remaining precipitate and solution were thrown upon a dry filter-paper, the filtrate received in a dry flask, and brought back to 20° C., when four 50 c.c. portions were drawn off, and labelled "filtrates." Throughout the investigation of chromium, manganese, and magnesium the same pipette was used.

Discussion.

For results see Table II.; also curves 7 and 8 in the plate. The chemical nature of adhesion is clearly shown here as well as in the case of iron, zinc, chromium, and aluminium. Experiment I. shows no sulphur trioxide in the precipitate, though the mass of precipitate is a maximum. Experiment II. shows that 15.34 per cent of the total sulphur trioxide is in the precipitate, while the mass of precipitate is some 9 per cent less than in Experiment I. Experiment III. shows 19.3 per cent of the total sulphur trioxide in precipitation, while the mass of precipitate is still less than in Experiment II. Experiment IV. confirms Experiment III., giving the maximum sulphur trioxide carried down. Experiment V. shows a falling off in the sulphur trioxide in precipitation, but if we remember how small the amount of precipitated manganous hydroxide is at this point (0.5 molecule KOH) the strength of the action is seen to be considerable.

No chlorine was carried down at 1.5 or 1.1 molecules of KOH ; hence this "adhesion" is seen to be selective—the sulphur trioxide is taken, and the chlorine left.

I think it probable that in absence of sulphur trioxide the chlorine would be carried down, since ferric hydroxide shows this same selective action, and does carry down chlorine in absence of sulphur trioxide.

Since in the case of iron, potassium appears in a precipitate only at 8 molecules of potassium hydroxide, and in the case of chromium, potassium does not appear at all up to 8 molecules of potassium hydroxide, it was considered unnecessary to determine potassium in the present investigation.

In the plate, I have plotted curves which show the per cent of oxide and of sulphur trioxide in the precipitates obtained by adding various amounts of potassium hydroxide to the chloride. Ordinates are in per cent of constituent; abscissæ, in molecules of potassium hydroxide required to produce the precipitate. Curve 1 is the per cent of total sulphur trioxide in the precipitate of ferric hydroxide; curve 2, the same for chromic hydroxide; curve 3, the same for ferric hydroxide—produced from a solution of ferric chloride having twice the concentration of that used for curve 1—(curves 1, 3, and 5 are taken from the thesis of V. J. Hall, *loc. cit.*). Curve 7 is the same for manganous hydroxide. Curve 4 gives the per cent of total chromium trioxide precipitated by varying amounts of potassium hydroxide in presence of a fixed amount of potassium sulphate. Curve 5 is the same for ferric oxide. Curve 6, the same for magnesium oxide—presence or absence of potassium sulphate has no effect on the trend of the curve. Curve 8, the same for manganese oxide. Curve 9, the same for zinc oxide

* From the *Journal of the American Chemical Society*, vol. xxv., No. 2.

Experi- ment.	KOH + $\frac{1}{2}$ K_2SO_4 .	"Total" MnO.	"Filtrate" MnO.	"Precipitate" MnO.	"Total" SO ₃ .	"Filtrate" SO ₃ .	"Precipitate" SO ₃ .	"Total" Cl.	"Filtrate" Cl.	"Precipitate" Cl.	"Total SO ₃ in "precipitate." Per cent.	"Total MnO in "precipitate." Per cent.
I.	2	0.2593	0.0146	0.2347	0.1381	0.1379 0.1368	0.0000	—	—	—	—	90.51
II.	1½	0.2593	0.04371	0.2122	0.1382	0.1186 0.1154	0.0212	0.3307	0.3335 0.3321	0.0000	15.34	81.83
III.	1½	0.2593	0.0833	0.1760	0.1376	0.1110 0.1111	0.0266	0.3298	0.3302 0.3340	0.0000	19.33	67.86
IV.	1	0.2593	—	—	0.1384	0.1103 0.1106	0.0270	—	—	—	19.50	—
V.	½	0.2593	—	—	0.1378	0.1244 0.1245	0.0133	—	—	—	9.65	—

TABLE II.

(C. E. Linebarger, *Journ. Am. Chem. Soc.*, 1895, xvii., 358). Curve 10 is the per cent of total sulphur trioxide in the precipitate whose remaining constituent is aluminium trioxide, the per cent of which is given in curve 11 (taken from Table VI., A. V. E. Young, *loc. cit.*).

My results as plotted in curve 7 show that the action of manganous hydroxide in carrying down sulphur trioxide into precipitation is truly chemical in nature, since the maximum carrying-down effect is observed far short of the maximum quantity of manganous hydroxide, as may be seen by reference to curve 8. The carrying down of chlorine and of potassium oxide remains to be investigated.* The results show, too, that the standard equations for the reaction between manganese chloride and potassium hydroxide, and between magnesium chloride and potassium hydroxide in aqueous solution, do not represent the facts (see curves 6 and 8; likewise, 9 and 11). The distribution of the constituents of these systems is dependent upon temperature, concentration, and the relative masses of the constituents. Further, the composition of the precipitates as given in the tables and curves considers the precipitate as anhydrous; unquestionably much water is combined in the gelatinous precipitates here studied, but owing to the lack of a method of getting at it quantitatively it has purposely been left unconsidered.

This work has a bearing on the subject of colloidal solution. Reference to a former paper will show that it is possible to form a colloidal solution containing chromium chloride, potassium chloride, and potassium hydroxide all combined with each other, and with water, so that the equation $2CrCl_3 + 3KOH = CrCl_3 + Cr(OH)_3 + 3KCl$ does not represent the true state of the system. If any soluble sulphate be added, this colloidal solution gelatinises. A nitrate or chloride will not produce this effect. It seems to me that this reaction disposes of the idea which had been advanced that any electrolyte will precipitate a colloid ("Chromic Hydroxide in Precipitation," *loc. cit.*). Here certainly the colloid seems to have a decided preference for sulphates.

Barium Sulphate.

To examine further this "adhesion" phenomenon, samples of barium sulphate were prepared in two ways:—(1) Precipitated with sulphuric acid from barium chloride dissolved in water, and the washed barium sulphate boiled for several hours with the aqueous solution of some metallic chloride. (2) Precipitated with sulphuric acid from an aqueous solution of barium chloride containing the same metallic chloride used in Method 1.

These samples enable one to decide whether the colouration of barium sulphate which is observed in samples precipitated in presence of salts of iron, manganese, chromium, &c., is necessarily enclosed when the crystal forms.

In this way I prepared samples of barium sulphate containing nickel, cobalt, manganese, chromium, iron, and copper, and examined them under a high-power microscope. The crystals were measured by a stage and eye-piece combination micrometer, and averaged 0.00005 to 0.000125 inch in diameter.

No difference in shade could be detected between barium sulphate crystals prepared by Method 1 and those obtained by Method 2 with any of the metals used. The colouration was well marked, and was compared with that of freshly prepared pure barium sulphate on the same glass slide.

These results indicate that the metals given can penetrate barium sulphate crystals after they are formed, and find lodgment there. But once these metals are in the barium sulphate crystal it is, as every analyst knows, no easy matter to get them out. From this we might, without doing violence, argue for chemical combination between the barium sulphate and the metal (or its salt or oxide).

* This work was done in 1896 and I have kept it back, hoping to make the data more complete; however, circumstances have not permitted of it, and do not at present. These results are of interest to those working on precipitation and solution, so I do not feel justified in withholding them longer.

Further, chromic chloride in aqueous solution is known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form), and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution, and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 12, September 21, 1903.

Properties and Constitution of Manganese Steels.—Léon Guillet.—The author continues his exhaustive study of manganese steels from the mechanical as well as the micrographical point of view. The experiments were performed on two series of very pure steels: the first containing 0.100 to 0.250 per cent of carbon, and the manganese increasing from 0 to 33 per cent; the second series containing 0.700 to 0.950 per cent of carbon, and the manganese varying from 0 to 12 per cent. The results obtained show the perfect coincidence between the metallographical and mechanical experiments. The author further establishes the great similarity existing between manganese and nickel steels. The "shock" experiments show clearly that less carburetted steels, and those containing less than 4 to 5 per cent of manganese, are not at all fragile. In a future paper he hopes to collect the present results in a simple diagram, similar to that obtained in the case of the nickel steels.

MISCELLANEOUS.

Regulations as to Milk-stores and Milk-shops, &c.—At a meeting of the Corporation of London, at the Guildhall of the City of London, on July 23, 1903, it was resolved:—That certain regulations with regard to the purveying of milk be approved and adopted, the said regulations to come into force on September 1st, 1903. The object of these regulations is to prevent the infection and contamination of milk within the City of London, and under them every purveyor of milk, dairyman, or cow-keeper must be registered as such. Rules are laid down with regard to the sanitary conditions of all dairies and cow-sheds, and the prevention of infection from any person engaged in the business, special attention being given to the maintenance of a pure and plentiful supply of water.

Oxidation by means of Fluorine set free by Electrolysis.—F. W. Skirrow.—On contact with water, fluorine produces ozone; in this manner the author has effected different electrolytic oxidations in the presence of dissolved hydrofluoric acid. Sulphate of chromium gave chromic acid; the manganous salts gave permanganates, and the return is much greater than in the presence of sulphuric acid. The salts of cobalt gave the sesquioxide. Experiments made with carbonic and sulphuric acids did not lead to any results. Hydrocarbons, such as benzene and naphthalene, are oxidised energetically in hydrofluoric solution, and more rapidly than in sulphuric solution.—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 25.

The Solubility of Boric Acid in Hydrochloric Acid.—W. Herz.—Contrary to the statements to be found in Dammer's Treatise on Chemistry, boric acid is less soluble in hydrochloric acid than in water. The following determinations were made at 26°. In hydrochloric acid of known strength, boric acid was dissolved until the saturation point was reached, then, on a known volume of the liquor, the total acidity was estimated, after the addition of mannite:—

HCl in molecules per litre.	B ₂ O ₃ in molecule per litre.
0.0	0.907
0.130	0.895
0.260	0.870
0.390	0.842
1.30	0.645
2.16	0.542
4.32	0.308
6.0	0.338
7.08	0.327
8.74	0.327
9.51	0.338

—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 355.

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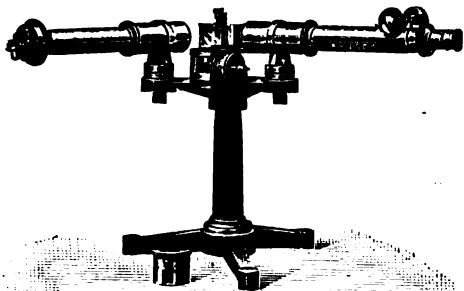
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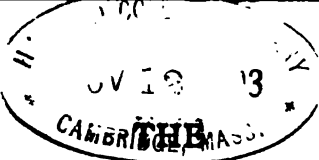
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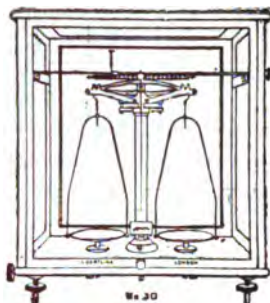
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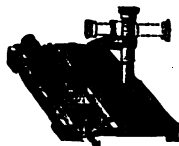
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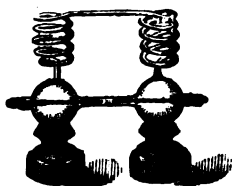
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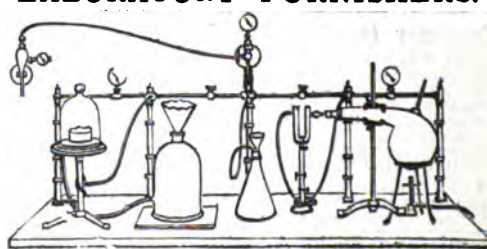
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2292.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 201).

CHAPTER III. (continued).

Ionising Action of Radium Rays on Insulating Liquids.

M. CURIE has pointed out that radium rays and Röntgen rays act upon liquid dielectrics as upon air, imparting to them a certain electrical conductivity. The experiment was carried out in the following manner (Fig. 9):—

The experimental liquid is placed in a metal vessel, CDEF, into which a thin copper tube, AB, is plunged; these two pieces of metal serve as electrodes. The outer vessel is maintained at a known potential, by means of a

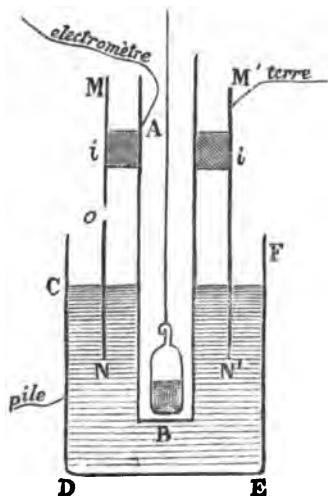


FIG. 9.

battery of small accumulators, one pole of which is connected to earth. The tube, AB, is connected to the electrometer. When a current traverses the liquid the electrometer is kept at zero by means of a quartz electrical piezometer, which gives the strength of the current. The copper tube, MNM'N', connected to earth, serves as a guard tube, preventing the passage of the current through the air. A bulb containing the radium-barium salt may be placed at the bottom of the tube, AB; the rays act on the liquid after having penetrated the glass of the bulb and the sides of the metal tube. The radium may also be allowed to act by placing the bulb beneath the side, DE.

In working with Röntgen rays the course of the rays is through side DE.

The increase of conductivity by the action of the radium rays or the Röntgen rays seems to be produced in the case of all liquid dielectrics; but in order to determine this increase, the conductivity of the liquid itself must be so slight as not to mask the effect of the rays.

M. Curie obtained results of the same order of magnitude with both radium rays and Röntgen rays.

When investigating with the same apparatus the conductivity of air or of another gas under the action of the

Bequerel rays, the intensity of the current obtained is found to be proportional to the difference of potential between the electrodes, as long as the latter does not exceed a few volts; but at higher tensions, the intensity of the current increases less and less rapidly, and the saturation current is practically attained for a tension of 100 volts.

Liquids examined with the same apparatus and the same radio-active body behave differently; the intensity of the current is proportional to the tension when the latter varies between 0 and 450 volts, and when the distance between the electrodes does not exceed 6 m.m.

The figures of the following table multiplied by 10^{-11} give the conductivity in megohms per c.c. :—

Carbon bisulphide	20
Petroleum ether	15
Amylene	14
Benzine	4
Liquid air	1.3
Vaseline oil	1.6

We may, however, assume that liquids and gases behave similarly, but that, in the case of liquids, the current remains proportional to the tension up to a much higher limit than in the case of gases. It therefore seemed probable that the limit of proportionality could be lowered by using a much more feeble radiation, and this idea was verified by experiment. The radio-active body employed was 150 times less active than that which had served for the previous experiments. For tensions of 50, 100, 200, 400 volts, the intensities of the current were represented respectively by the numbers 109, 185, 255, 335. The proportionality was no longer maintained, but the current showed great variation when the difference of potential was doubled.

Some of the liquids examined are nearly perfect insulators when maintained at a constant temperature and when screened from the action of the rays. Such are liquid air, petroleum ether, vaseline oil, and amylene. It is therefore very easy to study the effect of the rays. Vaseline oil is much less sensitive to the action of the rays than is petroleum ether. This fact may have some relation to the difference in volatility which exists between these two hydrocarbons. Liquid air, which has boiled for some time in the experimental vessel, is more sensitive to the action of the rays than that newly poured in; the conductivity produced by the rays is one-fourth as great again in the former case. M. Curie has investigated the action of the rays upon amylene and upon petroleum ether at temperatures of $+10^{\circ}$ and -17° . The conductivity due to the radiation diminishes by one-tenth of its value only, in passing from 10° to -17° .

In the experiments in which the temperature of the liquid is varied, the temperature of the radium may be either that of the surrounding atmosphere or that of the liquid; the same result is obtained in both cases. This leads to the conclusion that the radiation of radium does not vary with the temperature, and remains unaltered even at the temperature of liquid air. This fact has been verified directly by measurements.

Various Effects and Applications of the Ionising Action of the Rays Emitted by Radio-active Substances.

The rays of the new radio-active substances have a strongly ionising action upon air. By the action of radium the condensation of supersaturated water vapour can be easily induced, just as happens by the action of cathode rays and Röntgen rays.

Under the influence of the rays emitted by the new radio-active substances, the distance of discharge between two metallic conductors for a given difference of potential is increased; to put it otherwise, the passage of the spark is facilitated by these rays.

In causing conductivity, by the action of radio-active bodies, in the air in the neighbourhood of two metallic conductors, one of which is connected to earth and the other to a well-insulated electrometer, the electrometer is seen to be

* Thesis presented to the Faculté des Sciences de Paris.

permanently deflected, which gives a measure of the electromotive force of the battery formed by the air and the two metals (electromotive force of contact of the two metals, when they are separated by air). This method of measurement was employed by Lord Kelvin and his students, the radiating body being uranium; a similar method had been previously employed by M. Perrin, who was using the ionising action of Röntgen rays.

Radio-active bodies may be employed in the study of atmospheric electricity. The active substance is enclosed in a little box of thin aluminium fixed at the extremity of a metal wire connected with the electrometer. The air is made to conduct in the neighbourhood of the end of the wire, and the latter adopts the potential of the surrounding air. Radium thus replaces, with advantage, the flames or the apparatus of running water of Lord Kelvin, till now in general use for the investigation of atmospheric electricity.

Fluorescent and Luminous Effects.

The rays emitted by the new radio-active bodies cause fluorescence of certain substances. M. Curie and myself first discovered this phenomenon when causing polonium to act upon a layer of barium platinocyanide through aluminium foil. The same experiment succeeds yet more easily with barium containing radium. When the substance is strongly radio-active the fluorescence produced is very beautiful.

A large number of bodies are capable of becoming phosphorescent or fluorescent by the action of the Becquerel rays. M. Becquerel studied the effect upon the uranium salts, the diamond, &c. M. Bary has demonstrated that the salts of the metals of the alkalis and alkaline earths, which are all fluorescent under the action of luminous rays and Röntgen rays, are also fluorescent under the action of the rays of radium. Paper, cotton, glass, &c., are all caused to fluoresce in the neighbourhood of radium. Among the different kinds of glass, Thuringian glass is specially luminous. Metals do not seem to become luminous.

Barium platinocyanide is most conveniently used when the radiation of the radio-active bodies is to be investigated by the fluoroscopic method. The effect of the radium rays may be followed at distances greater than 2 m. Phosphorescent zinc sulphide is made extremely luminous, but this body has the inconvenient property of preserving its luminosity for some time after the action of the rays has ceased.

The fluorescence produced by radium may be observed when the fluorescent screen is separated from the radium by absorbent screens. We were able to observe the illumination of a screen of barium platinocyanide across the human body. However, the action is incomparably greater when the screen is placed immediately in contact with the radium, being separated from it by no solid screen at all. All the groups of rays appear capable of producing fluorescence.

In order to observe the action of polonium, the substance must be placed close to the fluorescent screen, without the intervention of a solid screen, unless the latter be extremely thin.

The luminosity of fluorescent substances exposed to the action of radio-active bodies diminishes with time. At the same time the fluorescent substance undergoes a transformation. The following are examples:—

Radium rays transform barium platinocyanide into a brown, less luminous variety (an action similar to that produced by Röntgen rays, and described by M. Villard). Uranium sulphate and potassium sulphate are similarly altered. The changed barium platinocyanide is partially regenerated by the action of light. If the radium be placed beneath a layer of barium platinocyanide spread on paper, the platinocyanide becomes luminous; if the system be kept in the dark, the platinocyanide becomes changed, and its luminosity diminishes considerably. But if the whole be exposed to light, the platinocyanide is partially regenerated,

and if the whole is replaced in darkness the luminosity reappears with vigour. By means of a fluorescent body and a radio-active body, we have therefore obtained a system which acts as a phosphorescent body capable of long duration of phosphorescence.

Glass made fluorescent by the action of radium becomes coloured brown or violet. At the same time its fluorescence diminishes. If the glass thus changed be warmed, it is decolorised, and when this occurs the glass becomes luminous. The glass has now regained its fluorescent property in the same degree as before the transformation.

Zinc sulphide, which has been exposed for a sufficient length of time to the action of radium, gradually becomes used up, and loses its phosphorescent property, whether under the action of radium or that of light.

The diamond becomes phosphorescent under the action of radium, and may thus be distinguished from paste imitations, which have only a very faint luminosity.

All the barium-radium compounds are *spontaneously luminous*. The dry anhydrous halogen salts emit a particularly intense light. This illumination cannot be seen in broad daylight, but it is easily visible in the twilight or by gas-light. The light emitted may be strong enough to read by in the dark. The light emitted emanates from the entire body of the product, whilst in the case of a common phosphorescent body, the light emanates specially from the portion of the surface illuminated. Radium products lose much of their luminosity in damp air, but they regain it on drying (Giesel). There is apparently conservation of luminosity. After many years no sensible modification is produced in the luminosity of feebly active products, kept in the dark in sealed tubes. In the case of very active and very luminous radium-barium chloride, the light changes colour after several months; it becomes more violet and loses in intensity; at the same time the product undergoes transformations; on re-dissolving the salt in water and drying it afresh, the original luminosity is restored.

Solutions of barium-radium salts, which contain a large proportion of radium, are equally luminous; this fact may be observed by placing the solution in a platinum capsule which not being itself luminous permits of the faint luminosity of the solution being seen.

When a solution of a barium-radium salt contains crystals deposited in it, these crystals are luminous at the bottom of the solution, and much more so than the solution itself, so that they alone appear luminous.

M. Giesel has made a preparation of barium-radium platinocyanide. When this salt is newly crystallised, it has the appearance of ordinary barium platinocyanide and is very luminous. But gradually the salt becomes spontaneously coloured, taking a brown tint, the crystals at the same time becoming dichroic. In this state the salt is much less luminous, although its radio-activity is increased. The radium platinocyanide, prepared by M. Giesel, changes still more rapidly.

Radium compounds are the first example of self-luminous bodies.

(To be continued).

New Publication.—A new journal dealing with chemical and physical science has been brought out recently in Geneva by M. Phillippe A. Guye, Professor of Chemistry at the University of Geneva. The primary object of this new venture is to facilitate the centralised publication of papers on physico-chemical subjects written in the French language, either *in extenso* or in an abridged form. In the second place, a bibliographic bulletin will be given at as early a date as possible, comprising an analysis of all papers on physical chemistry appearing in other languages, all the important works on these subjects published in other countries, and all the patents dealing with the special subjects of this new journal, which will be known as the *Journal de Chimie Physique*.

SILICIDES OF CHROMIUM.

By P. LEBEAU and J. FIGUERAS.

THE action of silicon on a metal in the presence of copper has enabled one of us to prepare in a state of purity the definite compounds formed by silicon with iron, cobalt, and manganese. We may mention that this method consists in reacting on a mixture of copper and the metal to be combined, with variable proportions of silicon in the form of silicised copper, free silicon, or of nascent silicon resulting from the action of sodium on an alkaline fluosilicate. Through the application of these different processes to the study of the binary compounds of chromium and silicon, we have succeeded in isolating the following four silicides:— SiCr_3 , SiCr_2 , Si_2Cr_3 , and Si_2Cr .

The silicide SiCr_3 is produced when we fuse a mixture of chromium and copper with a small quantity of silicon. An ingot containing—Cu 85.63, Cr 12.83, Si 1.24, gave, after alternate treatments with nitric acid and dilute soda, a residue consisting entirely of prismatic crystals of the compound SiCr_3 . In another experiment in which the mass melted had the following composition:—Cu 84.32, Cr 10.83, Si 4.36, this same silicide, SiCr_3 , still remained perfectly homogeneous after the attack.

Above this proportion of silicon, and with quantities of chromium and silicon very similar in amount, we observe, besides the crystals of SiCr_3 , other very different crystals, having brilliant facets in the form of a lozenge. They constitute the silicide SiCr_2 . By the treatment of an ingot containing—Cu 78.22, Cr 12.04, Si 8.92, this compound has been isolated in a very pure state.

In following up the study of the fused products containing increasing quantities of silicon, we find, in the residues, new crystals formed of very brilliant prisms, differing most decidedly from the thickest crystals of SiCr_3 . With the following proportions:—Cu 83.84, Cr 3.03, Si 12.92, we obtain a very homogeneous residue of long prisms, answering to the formula Si_2Cr_3 .

Finally, as the proportion of silicon increases in the products of fusion, we observe the formation of a fourth compound in small crystals of a deep colour and much less brilliant than the preceding ones. Further, these latter disappear completely, and with high proportions of silicon we only find, as a result of the attack with nitric acid, the fourth variety mixed with free silicon, which can be eliminated by means of soda. This body is the chromium compound richest in silicon, and answers to the formula Si_2Cr .

Among these four silicides of chromium two have been described already; the silicide SiCr_3 was obtained by M. Zettel (*Comptes Rendus*, vol. cxxvi., p. 833), and the silicide SiCr_2 was prepared and examined by M. Moissan (*Ann. Chim. Phys.*, 171, vol. ix., p. 289). As for the compound Si_2Cr , it was announced by M. de Chalmont (*Ann. Chim. Phys.*, vol. xix., p. 69), but this chemist did not succeed in extracting it from the matrix in which it was formed. Only the silicide Si_2Cr_3 is entirely new; we will therefore describe its preparation and principal properties.

Preparation of the Silicide of Chromium, Si_2Cr_3 .—It is prepared the most easily by heating in the electric furnace in a carbon crucible, a mixture of 100 grms. of silicide of copper at 12 per cent, with 4 grms. of chromium. The time of heating should be about four minutes, with a current of 600 amperes and 70 volts. The resulting ingot should weigh approximately the theoretical amount. It is broken up and attacked with nitric acid at 50 per cent, taking care to alternate with washings with commercial soda-lye diluted with ten times its volume of water. When these reagents no longer dissolve anything, wash with water and dry in the oven.

The above mixture may be also melted over a forge. The cooling is slower in this case, and much better formed crystals are obtained.

Properties of the Silicide Si_2Cr_3 .—The silicide Si_2Cr_3 crystallises in long quadrangular prisms, rarely terminated.

Its density at 0° is 5.6. It scratches glass, but will not mark quartz.

Chlorine reacts on this compound at about 400° , giving chromic chloride and chloride of silicon; bromine attacks it more slowly at a cherry-red heat; under the same conditions iodine is without any action.

The silicide of chromium is unoxidisable in the air, either dry or moist, in the cold. At a temperature of 1100° it becomes covered with a very thin iridescent layer which prevents any further action of the oxygen.

Hydrochloric acid gas decomposes it, with the production of chromous chloride. A solution of dilute hydrochloric acid has no action in the cold on this silicide; a concentrated solution dissolves it with the greatest ease if gently heated. Nitric and sulphuric acids are without action, but hydrofluoric acid attacks it almost immediately.

Fused nitrate and chlorate of potassium, both of which react energetically on the carbides of chromium, have no effect on this silicide; on the other hand, with the alkaline carbonates it is rapidly transformed into an alkaline silicate and oxide of chromium. If we add a nitrate, a mixture of alkaline silicate and chromate is formed. This latter reaction, as well as that of hydrochloric acid, has been utilised for its analysis:—

	Found.	Theory.
Si	26.32, 26.81, 26.40	26.65
Cr	74.11, 73.64, 73.33	73.34

It should be remarked that the compounds of chromium and silicon do not show the analogies of formula that one of us has already described for the silicides of iron, cobalt, and manganese. These metals each furnish, in fact, three compounds corresponding to the types— SiX_2 , SiX , and Si_2X . With chromium there are certainly the silicides SiCr_2 and Si_2Cr , but there are also two bodies with formulæ which are not comparable, viz., SiCr_3 and Si_2Cr_3 .—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 15.

PURIFICATION OF THE SULPHURETTED HYDROGEN USED FOR THE DETECTION OF ARSENIC.

By ARMAND GAUTIER.

To precipitate arsenic from its acid solutions in the state of sulphide Selmi used sulphuretted hydrogen produced by the decomposition of the alkaline or alkaline-earthly sulphides by hydrochloric acid.†

I have not specially examined the gas thus produced, having found it more practicable to purify ordinary sulphuretted hydrogen. It always contains arsenic, particularly in the form of arseniuretted hydrogen, resulting from the metal in the sulphide; arseniuretted hydrogen that is not decomposed by sulphuretted hydrogen, and that four or five washings with acid or water will not remove completely. A moderate current of ordinary sulphuretted hydrogen gas washed in this manner, passing a bubble at a time for two hours through nitric acid heated to 80° , gave me 0.08 m.grm., or nearly a tenth of a milligram. of arsenic.

To purify sulphuretted hydrogen I tried passing the impure gas through a tube heated to dull redness. The arsenic is deposited principally in the front part of the tube, with a little sulphur coming from the sulphuretted hydrogen; but it is not yet pure. It still gives, after passing

* We have extended our researches to the silicised compounds of nickel, but these latter having less resistance to the action of acids their separation is much more difficult. In any case, the series of these silicides seems to be of the same type as that of the silicides of cobalt, manganese, and iron.

† I have observed that sulphuretted hydrogen passed, first hot and then cold, through an arsenical solution containing from 1 m.grm. to 0.002 m.grm. of arsenic, precipitates the whole of this metalloid so completely that the filtered liquor no longer contains the slightest trace.

through warm nitric acid for two hours, a ring of 0.004 m.grm. of arsenic.

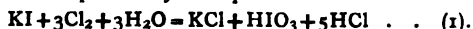
For its complete purification, the sulphuretted hydrogen gas, first washed with water, is passed through a vertical column of 30 c.m. of moist pumice stone, then through a combustion-tube filled with fragments of glass and heated to dull redness for a distance of 25 c.m. The gas is then passed through one of my serpentine bulb-tubes filled with a concentrated solution of sulphide of barium, when it again deposits traces of arsenical compounds. Finally, it is passed through a tube packed with cotton-wool before arriving at the liquor in which it is to react. Thus purified, this gas, after a passage, bubble by bubble, through boiling nitric acid, which oxidises the whole, gave me a total amount of arsenic of 0.0008 m.grm. Not a trace could be found when 300 to 400 c.c. of this gas were passed through acidulated water.

If we pass a current of impure sulphuretted hydrogen, simply washed in a series of acid and water bulbs, through an acidulated aqueous solution of 300 or 400 c.c., such as that obtained by treating by my method the azotised carbon resulting from the destruction of organic matter; in this liquor we find, after two hours, from 0.001 to 0.0006 m.grm. of arsenic, instead of the 0.080 m.grm. contained by the whole of the gas as shown above. Impure sulphuretted hydrogen introduces an error of not less than 1 m.grm. in the result—an error which is of considerable magnitude in an estimation of such delicacy.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

TITRATIONS WITH POTASSIUM IODATE.

By LAUNCELOT W. ANDREWS.

As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation—



On the other hand, it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be—



In both cases the end of the reaction is shown by the immiscible solvent becoming colourless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation—



while if a great excess of hydrochloric acid is present the reaction runs—



the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colourless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behaviour is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus—



the iodic hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, &c., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré (*Liebig's Ann. Chim.*, 1855, xciv., 365) for the titration of iodides. In order to compare the reactions

of the first two equations, I titrated 5 c.c. of a decinormal potassium iodide solution with chlorine water in presence of 5 c.c. of chloroform. After the addition of 75.4 c.c. of the latter the chloroform became colourless. The titration was now repeated with the further addition of respectively 15, 20, and 30 c.c. of strongest hydrochloric acid, and the amounts of chlorine water required were 25.4, 25.22, and 25.25 c.c., the end reaction being of extraordinary sharpness. Nearly three times as much chlorine was therefore required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (Equation 1) had been neutralised by the addition of calcium carbonate the theoretical amount of 75.75 c.c. of chlorine solution would have been required. In order to judge the influence of smaller quantities of acid, the titration was repeated with addition of 1, 2, 5, and 10 c.c. of concentrated hydrochloric acid, when respectively 34.1, 26.9, 26.0, and 25.6 c.c. of chlorine water were required.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid, and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realising the reaction of Equation 4. 9.7465 grms. of acid potassium iodate were dissolved in water and made up to 1 litre. According to the theory, each c.c. of this solution should be equivalent to 16.6 m.grms. of potassium iodide. To 10 c.c. of a solution of pure potassium iodide (20.6 grms. to the litre), 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of concentrated hydrochloric acid (sp. gr. 1.21) were added, and the mixture was titrated in a glass-stoppered bottle of 250 c.c. capacity, with the iodate solution, shaking briskly, until the chloroform lost its colour, the end-point being exceedingly sharp. 12.43 c.c. of the iodate solution were required. Hence, 0.20634 grm. potassium iodide was found against 0.20600 taken, or 100.17 per cent. In a second experiment, 15 c.c. of the iodide solution, titrated in the same way with 33 c.c. of hydrochloric acid and no additional water, required 18.62 c.c. of the iodate solution, corresponding to 0.30900 grm. found, against 0.30900 grm. taken, or 100.00 per cent taken.

The process as described can be applied to the titration of chromates. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 c.c. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36.3 m.grms. of potassium pyrochromate were taken, and 36.8 m.grms. found.

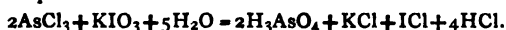
The following experiment shows the applicability of the process to the titration of free iodine:—0.3447 grm. of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 c.c. of a potassium iodide solution containing 20.6 grms. per litre; 10 c.c. of fuming hydrochloric acid, and 5 c.c. of chloroform were added, and the titration was carried out in the usual way. Required, 19.85 c.c. of standard iodate. Since 6.20 c.c. are required for the iodide, 13.65 c.c. remain as corresponding to the free iodine, or 0.3467 grm. iodine found; 100.46 per cent.

To determine whether the method can be used for determination of chlorates, and under what conditions, the succeeding experiments were tried. Five c.c. of a solution of potassium chlorate containing 70.3 m.grms. of the pure salt was added to 25 c.c. of the potassium iodide solution mentioned above, and 50 c.c. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 c.c. of chloroform were added, and the titration completed. Required, 13.65 c.c. of the iodate. As the iodide is equivalent to 31.0 c.c., 17.35 c.c. correspond to the chlorate, whence 70.9 m.grms. of potassium chlorate were found. In a second similar experiment, only 40 c.c. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 13.98 c.c. of iodate were required, hence 69.55 m.grms. of chlorate were found.

This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment, exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13.77 c.c. of iodate were required, whence 70.41 m.grms. of chlorate were found. It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 c.c. of another potassium chlorate solution containing 33.46 m.grms. of the pure salt was allowed to stand for ten minutes with 10 c.c. of iodide solution, and 20 c.c. of fuming hydrochloric acid; then 5 c.c. of chloroform were added, and the titration was performed. Required, 4.23 c.c. of iodate. Calculated for the iodide, 12.40 c.c., whence 33.39 m.grms. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a chlorate can be prescribed as follows:—

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the volume of the solution. Close the bottle tightly, and allow it to stand fifteen minutes after shaking, then add 5 c.c. of chloroform. On now shaking, the chloroform must become deep violet. If the colour is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colourless, which point can be estimated with the utmost precision. Each c.c. of a decinormal iodate solution is equivalent to 2.782 m.grms. of (ClO_3) .

Solutions of arsenious acid or chloride can be titrated in the same way as iodides, the reaction being expressed by the equation—



In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent does not. On the other hand, the minimum limit is in the neighbourhood of 12 to 15 per cent of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken, 25 c.c. arsenious solution (243.8 m.grms. As_2O_3) and 50 c.c. of fuming hydrochloric acid; required 24.45 c.c. decinormal = 242.1 m.grms. of arsenious oxide. Taken, 5 c.c. arsenious solution, 5 c.c. hydrochloric acid, and 10 c.c. water; required, 4.91 c.c. of iodate = 48.6 m.grms.; found, 48.8 m.grms. by iodine titration. Taken, 20 c.c. arsenious solution and 40 c.c. hydrochloric acid; required, 19.69 c.c. iodate = 194.9 m.grms. arsenious oxide; found, 194.7 m.grms. by iodine titration. Taken, 15 c.c. arsenious solution and 30 c.c. hydrochloric acid; required, 14.79 c.c. iodate = 146.4 m.grms. arsenious oxide; found, 146.3 m.grms. by iodine titration.

To summarise, add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent of the entire mixture at the end of the titration, and 5 c.c. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite, shake well, and continue titrating with the iodate until the chloro-

form is colourless. Each c.c. of the stand solution corresponds to 9.9 m.grms. arsenious acid or 7.5 m.grms. arsenic.

The determination of antimony is precisely like that of arsenic. A solution was prepared of pure re-crystallised antimonyl tartrate, containing 31.251 grms. per litre. Twenty-five c.c. of this were mixed with 30 c.c. hydrochloric acid and 20 c.c. water, and titrated as usual. 23.62 c.c. of the iodate were required, equivalent to 784.6 m.grms. tartar emetic found as against 781.3 m.grms. taken. In this determination the amount of hydrochloric acid should have been greater by 15 c.c. In the next experiment, 25 c.c. of the antimonious solution with 25 c.c. of hydrochloric acid required 23.50 c.c. of iodate, equivalent to 780.6 m.grms. of antimony salt found (781.3 taken). Twenty-five c.c. antimony solution with 35 c.c. fuming hydrochloric acid required 23.54 c.c. of iodate, whence is calculated 781.2 m.grms. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the arsenic in Paris green directly without preliminary separation. Thus, 20 c.c. of a sodium arsenite solution with 20 c.c. of fuming hydrochloric acid required 8.95 c.c. of iodate, the same, plus 1 grm. of copper sulphate, required 9.00 c.c. of iodate. For the analysis of Paris green, 0.5 grm. of the substance is dissolved in 15 c.c. of water and 25 c.c. of fuming hydrochloric acid, and directly titrated with 5 c.c. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken, 2.0874 grms. ammonium ferrous sulphate; required, 26.06 c.c. iodate, equivalent to 297.6 m.grms. iron found, or 14.26 per cent; theory, 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with this determination. Taken, 2.0843 grms. ammonium ferrous sulphate and 1 grm. oxalic acid; required, 25.95 c.c. iodate, equivalent to 296.3 m.grms. iron, or 14.22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow, and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

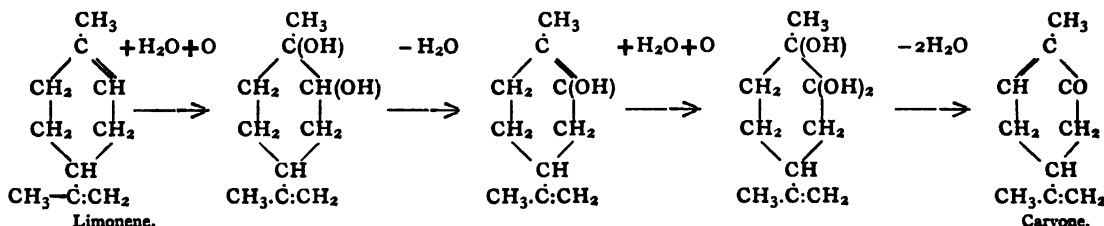
The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.—*Journal of the American Chemical Society*, vol. xxv., No. 7.

Action of different Metallic Powders on Carbonic Oxide.—Paul Sabatier and J. B. Senderens.—The authors have tried the action of heated nickel, cobalt, and iron in powder on carbonic oxide. They find that, with nickel and cobalt, there is a catalytic decomposition of the oxide of carbon, and this may be explained in several ways. The authors are not of the opinion that the cause can be attributed to a purely physical action of the condensation of the gas, due to the porous condition and the large surface of the metals formed by reduction; platinum-black, which is generally so efficacious, has no action in this case. The cause appears to be, as in most similar phenomena, the formation of temporary, unstable compounds, the intermediate production of which determines the principal reaction.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 8.

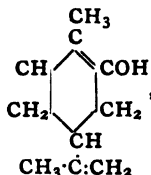
ESSENTIAL OILS.*

By Dr. O. SILBERRAD.

THE production of essential oils, although of extreme antiquity, has only recently been made the subject of scientific research. The earlier methods of extraction from the plants were exceedingly crude, and it was only in the early part of the Nineteenth Century that the industry received a new impulse by the introduction of steam distillation for the recovery of these essences. Chemical research has in recent years led to the replacement of the natural oils to some extent by products artificially prepared. As an instance of this, the author's recent discovery that carvone, $C_{10}H_{14}O$, the active principle of caraway oil, could be obtained direct from limonene by autoxidation was referred to. The mechanism of the reaction is probably expressed as follows:—



The above explanation is confirmed by the fact that the author has recently succeeded in isolating a monatomic alcohol as an intermediate product, to which he assigns the formula—



which corresponds to the hitherto unknown carvol. A specimen of the acetate of this alcohol was exhibited.

Other instances investigated by the author are the active principles of ylang-ylang, neroli, carnation, and oil of myrrh.

The specimens shown illustrate how nearly the synthetic products approach to the natural perfumes. A new and much more economical method for the manufacture of terpineol, recently discovered by the author, was briefly referred to. One great advantage claimed for this method was that the ingredients generally considered necessary for the reaction are replaced by much less costly reagents.

The author then went on to consider the various ways of obtaining essential oils, and showed that the methods of extraction differ for the various natural oils.

I. Turpentine, the source of terpineol, is obtained from pine trees in America by the process of "boxing," succeeded by steam distillation. Venetian turpentine is obtained by drilling holes in the trees, whilst Strasbourg and laurentine turpentine is still collected in certain districts by means of small pointed cans.

II. A second method is that of direct distillation from the plant, used, for instance, in the preparation of camphor and the recovery of camphor oil from the wood of *Laurus camphora* in Japan. Further treatment of the distillate leads to its separation into camphor, light camphor oil (mainly pinene, phellandrene, and dipentene), and heavy camphor oil, which latter is interesting as the source of saffrol, from which piperonal is now commercially obtained under the name of heliotropine. Investigations by the author have facilitated this conversion of saffrol into isosaffrol, and very considerably reduced the cost of production of heliotropine.

The conversion of saffrol into vanilline by treatment with sodium methylate and subsequent oxidation is also interesting; the chief source of vanilline is, however, eugenol obtained from oil of cloves. Eugenol is associated in oil of cloves with a sesquiterpene cariophyllene from which the author has recently obtained an acid containing eleven carbon atoms. (A specimen of this acid was exhibited).

III. A process of expression is used for the extraction of oils which are decomposed by steam, such as bergamot (linalool acetate). The artificial preparation of this ester presents considerable difficulties, as linalool undergoes decomposition or isomerisation on coming in contact with acids, and gives only very small yields of the desired esters, but investigations by the author have led to its manufacture on a commercial scale. A laboratory method whereby the difficulty may be overcome, worked out by the author, was also described, and consisted in treating a pyridene solution of the alcohol with the required acyl chloride. The in-

vestigation of linalool has hitherto laboured under the difficulty that no solid derivative of this alcohol could be obtained. It is hoped that the author's recent preparation of a crystalline compound of linalool—the hexanitro-diphenylurethane—will be of assistance in this direction. Geraniol, an isomer of linalool, is important as the chief ingredient of otto of roses. Its acetic and butyric esters are also valuable as scents.

A fourth and very ancient method for the extraction of essential oils is illustrated by jasmine oil, which is obtained by exposing the flowers over odourless petroleum, whereby the perfume is absorbed and subsequently extracted with acetone. This oil is a mixture of a number of compounds, the distinctive odour being, however, due to jasmone, which is present to only a small extent in the oil. Peach oil contains also a large number of constituents; among these the author has isolated the ethyl ester of an undecylenic acid, the presence of which is interesting as being a case of the natural occurrence of a fatty acid containing an odd number of carbon atoms.

The sesquiterpene alcohol, santalol from sandal-wood oil, irone from orris oil, the oxygenated products from orange oil, lemon oil, and lime oil were briefly treated of. The specimens of these various compounds illustrated their valuable properties as perfumes. A few brief remarks throughout the paper illustrated the costliness of these oils; thus it was shown that about three tons of roses were required to yield one pound of otto; the cost of peach oil is between three and four times as great, whilst to prepare one pound of jasmone about 200 tons of jasmine flowers would be required.

Research on the $\alpha\beta$ -Dimethylglutaric Acids.—E. E. Blaise.—This research has had a double object—the synthesis of the $\alpha\beta$ -dimethylglutaric acids, and the verification of certain theoretical questions as to whether tiglic acid can give synthetically only one racemic or not, the other one being furnished by angelic acid. In the end the author found that, contrary to expectation, both angelic and tiglic acids give the same product of condensation. It must be mentioned, however, that the dimethylglutaric acid obtained from angelic acid appeared to be less pure, and seemed to contain a small quantity of an isomer, probably liquid, and which could not be isolated in the pure state.—*Bull. Soc. Chim.*, S8ries 3, vol. xxix., No. 8.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING SEPTEMBER 30TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, October 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, 209 were clear, bright, and well filtered, and two samples were slightly turbid.

The rainfall at Oxford during September shows a deficit. The actual amount of rain measured was 1.54 inches; the average for the month is 2.39 inches, leaving a deficit of 0.85 inch, which, subtracted from the previous excess of 9.77 inches, leaves a total excess for the first nine months of the year of 8.92 inches. This is 49.3 per cent above the average for the past thirty-five years.

As autumn approaches, all natural surface waters, like the supplies from the valleys of the Thames and Lea, begin to show an increased amount of vegetable matter in solution. In spite, however, of there being less rainfall during September, the soluble organic matter has increased, although it still remains below the amount present during the month of June.

Our bacteriological examinations of 369 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 418 others from special wells, standpipes, &c., making a total of 787 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	333
New River, filtered (mean of 74 samples) ..	19
Thames, unfiltered (mean of 25 samples) ..	6202
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 195 samples) ..	39
Ditto ditto highest	496
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	330
River Lea, from the East London Water Com- pany's clear-water wells (mean of 25 samples)	29

Of the 294 daily samples taken from the filter wells of the Metropolitan Water Companies, seven samples, or 2.4 per cent, were sterile. There were twenty-seven samples, or 9.1 per cent, containing more than 100 microbes, and of these, ten samples contained more than 150 microbes per c.c. The twenty-seven excess samples contained an average of 182 microbes per c.c.; in August thirty-eight excess samples contained an average of 180 microbes per c.c.

The general result of the month's chemical and bacteriological examination is to show that while the organic carbon has increased, the microbic impurities have diminished. Efficient filtration has been well maintained considering the exceptional season.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE COLOURS OF IODIDES.*

By WILLIAM ACKROYD, F.I.C.

THE general law of the relation of colour to chemical constitution was stated by the author in 1892 (CHEMICAL NEWS, 1893, lxxvii., 27). Briefly it is that in related compounds of the general formula, A_xB_y , as B increases in weight (either in atomic mass or multiple of atomic mass) there is increase of absorption of light in definite manner, so that the visible effect is progression in the metachromatic scale from the white towards the black end. With one colour vision this would appear like a gradual darkening—an aspect of the phenomenon which the author ("On Opacity to the Röntgen Rays," W. Ackroyd and H. B. Knowles, *Journ. Soc. Dyers and Colourists*, April, 1896, vol. xii.) regards as being presented by X-rays in the photographic effects produced by them after passing through equal thicknesses of the members of a series A_xB_y . That this generalisation is reasonably fact-embracing is seen when it is stated that there are only about 2.27 per cent of exceptions in a survey of some 616 correlated inorganic coloured compounds, and many of these exceptions are of a doubtful nature.

Iodides conform to the law; the more heavily weighted molecules have colours nearer the black end of the scale; while the lighter ones, on the other hand, come nearer the white end. Thus in vertical series of the periodic classification arsenic tri-iodide is orange as compared with the red of antimony and bismuth tri-iodides; magnesium, zinc, and cadmium iodides are white, while mercuric iodide is yellow or red. In the periodic groups there are forty-one examples of iodides; only three are apparently uncomformable, two of these being doubtful exceptions.

When there is more than one iodide of the same metal we have again conformity to rule, thus:— Hg_2I_2 is olive green, and HgI_2 yellow or red.

The iodides have also a normal colour when compared with the other halides of the same radical as in the series AsF_3 , $AsCl_3$, $AsBr_3$, and AsI_3 . In the tabulation of these relations conformity to the law is seen both in horizontal as well as vertical groups, and 270 colour facts are presented in such a tabulation which give less than 3 per cent of exceptions.

Finally, the result of recent research shows that the element iodine has also a normal colour among the other liquid and solid halogens; their absorption increases from fluorine to iodine through the extremes of white to black.

It is amply apparent, therefore, that in a comparable series of compounds having similar molecular structure as represented by the same general formula, we may have colourless or white bodies at one end and coloured substances at the other end. Hence it is contended that Professor H. E. Armstrong's view that colour is an indication of "quinonoid" structure does not hold for iodides as maintained by Miss I. Smedley (*Brit. Assoc. Report*, 1902, p. 582), nor for inorganic bodies generally.

Tables are given illustrating these various observations.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

SYNTHESIS OF GLUCOSIDES.*

By W. SLOAN MILLS, M.A., Queen's College, Glasgow
(1891 Exhibition Scholar).

THE first known instances of the synthesis of a glucoside occurring in nature was effected by Michael, who, having prepared helicin from acetochloroglucose and sodium salicylic aldehyde in absolute alcohol solution, reduced it with sodium amalgam, and obtained salicin. Eugenol and phenol glucosides and also methylarbutin were prepared by Michael (*Comptes Rendus*, 1879, lxxxix., 355; and *Am. Chem. Journ.*, v., 6, 336). His method was somewhat modified by Ryan (*Journ. Chem. Soc.*, 1899, lxxv., 1054), who prepared *o*- and *p*-cresol glucosides, and also carvacrol glucoside, which contains an unchanged phenolic hydroxyl group. Glucosides of the alcohols and mercaptans have been prepared by Fischer (*Ber.*, 1893, xxvi., 2400; 1894, xxvii., 674, 2483, 2985) by the action of the alcohol or mercaptan on the sugar in presence of hydrochloric acid. A series of crystalline α - and β -acetochloro and acetobromo glucoses have recently been obtained by Fischer and Armstrong (*Ber.*, 1901, xxxiv., 2885), by which the synthesis of many alkyl and phenol glucosides has been effected. They have also prepared acetodibromoglucose, which Professor Fischer allowed me to use with a view to preparing glucosides containing a bromine atom in the glucose rest, and also amidoglucosides.

Preparation of Phenolbromoglucoside,
($C_6H_5O(OH)_3.Br.O.C_6H_5$).

A solution of potassium phenolate in absolute alcohol was allowed to act on a solution of acetodibromoglucose in chloroform for fourteen days. The solution was filtered, and the residue obtained on spontaneous evaporation was neutralised with acetic acid and extracted with ether. When the ether was evaporated a residue was obtained which, when re-crystallised from dilute alcohol, gave beautiful white needle-shaped crystals of phenolbromoglucoside, melting at 165° C. The glucoside reduces Fehling's solution. It is easily soluble in ether, acetone, and ethylacetate, soluble in alcohol, and somewhat soluble in chloroform. It is easily soluble in concentrated sodium hydroxide, and the solution, when carefully neutralised, gives a precipitate which melts at 170–180° C., and which reduces Fehling's solution only after being hydrolysed by boiling with dilute acids. The bromine in phenolbromoglucoside is not precipitated by silver nitrate solution.

It is hoped to replace the bromine atom in this compound by an amido group, and then by splitting off the phenol rest to obtain an amidoglucose, and thus determine the position of the second bromine atom in acetodibromoglucose.

PRELIMINARY NOTE ON SOME ELECTRIC
FURNACE REACTIONS UNDER HIGH GASEOUS
PRESSURES.*

By J. E. PETAVEL and R. S. HUTTON.

AN account was given of work carried out in the electrochemical laboratory at Owens College with an inclosed electric furnace constructed to work with gaseous pressures up to 200 atmospheres. The power employed has been usually about 15 kilowatts per hour, the furnace containing a charge of about 20 lbs. of material, and 1000 to 2000 litres of gas. A second furnace of about one-tenth the capacity was used for gas reactions with high-tension current.

The reactions at present under investigation include the direct reduction of alumina by carbon, the condition of formation of calcium carbide, particularly as modified by the change of gaseous atmosphere, and the formation of

graphite. With regard to gaseous reactions a study of the production of nitric acid and cyanogen compounds has already been commenced.

The preliminary experiments have shown that under pressure alumina is reduced to the metallic condition, but in all cases accompanied by a large amount of aluminium carbide. This reaction is most unfavourably influenced if the carbon monoxide which is formed be retained, whereas it is favoured by the rapid removal of the gaseous products of reaction. So far as calcium carbide is concerned, contrary to expectation, the yield is in no way diminished by the presence of carbon monoxide gas even at high pressures. An important difference in the methods of working is necessary in those cases where it is desired to effect purely gaseous reactions. Here a high-tension current is required. For instance, the formation of nitric acid, even at pressures of 100 atmospheres, is only accomplished in appreciable amount where the electromotive force used is of several thousand volts.

A general description was also given of the plant employed for preparing and compressing the various pure gases required in quantity for this work.

NOTE ON THE RATE OF COMBUSTION
AND EXPLOSIVE PRESSURE OF CORDITE.*

By J. E. PETAVEL.

THE research of which a preliminary account was given is being carried out in the physical laboratories of the Owens College.

The subjects under investigation are:—The effect of the diameter of the cordite, of the charging density, and of the shape of the enclosure.

The curves of rise and fall of pressure are for each explosion automatically recorded; the high pressure recorder described at a previous meeting being used for this work (see *Report Brit. Assoc.*, Glasgow, 1901, p. 768; and *Phil. Mag.*, May, 1902).

Attention was drawn to the dangerous vibrations which are set up when the charge is not uniformly distributed throughout the enclosure.

Action of Boiling Caustic Lyes on Picric Acid.—E. Wedekind and J. Haeussermann.—It has been observed some time ago that picric acid or its salts, by the action of boiling alkalis, undergo decomposition to a more or less considerable extent; that on boiling a solution of picrate of barium in caustic baryta hydrocyanic acid is formed, and that solutions of picric acid in an excess of alkali give off a small quantity of ammonia. The authors have endeavoured to follow up and define these reactions; they have observed that on heating for eight hours with a large excess of soda, potash, or baryta lye there is about 5.9 per cent of ammonia formed, or decidedly less than one molecule. When the solution is made acid a slight odour of hydrocyanic acid is observed; this proves that a small portion of the nitrogen has escaped transformation into ammonia. Further, a considerable amount of oxides of nitrogen is formed, which shows that the alkaline picrates heated in the presence of an excess of alkali give rise to the formation of alkaline nitrate, as suspected by the authors. They have shown, by estimations of the NO, that a nitro group of the picric acid is eliminated in the form of nitrite, and that the action of the above three lyes is quantitatively different, contrary to what was found in the estimation of the ammonia. After having eliminated the oxide of nitrogen, the authors have not been able to isolate from the product of the reaction, which is a solid homogeneous substance, anything else than unchanged picric acid in small quantities. The chemical reaction involved is probably very complicated.—*Berichte*, vol. xxxv., p. 1133.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, Wednesday, August 5, 1903.

F. B. GUTHRIE, F.I.C., F.C.S., President, in the Chair.

"On the Protection of Iron and other Metal Work." By WILLIAM M. HAMLET, F.I.C., F.C.S., Government Analyst.

The author pointed out that the stability and permanence of the materials used in building construction depended on the application of a knowledge of chemistry and physics, and that the engineer, architect, and builder must keep in touch with this knowledge in order to make the best use of the nature and possibilities of their materials; and just as the chemist seeks a knowledge of the structure and disintegration of matter, so also will he know of the best means to adopt for the protection of materials against the wear and tear of atmospheric and other influences. Any given structure, whether it be a ship, an engine, a house, or a bridge, will, if left to itself, become weathered, perish, and decay unless protected. The many hosts to be thus reckoned with are:—Chemical and electrical influences, mechanical and meteoric changes, erosion by sand, wind, and rain, factory chimney emanations, all more or less accelerated by contraction and expansion, together with biological influences and animal depredations.

It is found that by examining the structure of a metal much useful information may be obtained as to its powers of resistance under given circumstances. A section of a metal, for instance, is highly polished and then etched by an acid, an alkali, or a peroxide, either applied directly or by electrolytic methods. From the visible grain, texture, or structure, as seen under the microscope, good and bad materials may be differentiated one from another.

This method of examination and testing materials has come rapidly into use during recent years, and is particularly useful in the case of iron, steel, bronze, brass, Muntz, and other yellow metals.

The rusting of iron and steel is dealt with, the author referring to experiments made from time to time during the last fifteen years, and the immediate cause of the publication of this paper at the present time was owing to a paper published in a recent number of the *Journal of the Chemical Society* by Dunstan, followed by a similar one by Moody on the rusting of iron. The former observer lays stress on the action of hydrogen peroxide, while the latter accounts for rust by the action of carbonic acid, which action he compares to the action of any mineral acid on iron, with the consequent liberation of hydrogen. Petit, in 1896, showed that the mere presence of carbonic acid gave rise to corrosion and formation of ferrous carbonate, which is one of the antecedent products in the formation of rust.

The author was engaged in a work of investigating the causes of the rapid corrosion or rusting away of the iron casing at one of the Australian artesian bores, where abundance of carbonic acid gas was evolved at the rather high temperature of 100° F.; the water also contained alkaline carbonates and bicarbonates with sodium chlorides, silica, &c., amounting to between 30 and 40 grains of total solid matter to the gallon. This is an admittedly difficult case to deal with, and probably a specially hard and resistant alloy will be required to stand the prolonged and severe action of the water in question.

The protection of ironwork under usual conditions is best effected by the use of a paint or an enamel having a coefficient of expansion equal or nearly equal to that of the iron itself, so that cracking or bursting of the skin of paint shall be prevented, which would otherwise lead to exposure of the bare iron to outside influences. Dr. Angus Smith's composition, the Bower-Barff process, red-lead, iron oxide, asphalt, and graphitic paints were each considered, the author holding a high opinion of simple pure red-lead and

genuine linseed oil as an excellent covering for most purposes. Galvanised iron, lead, bronze, Muntz metal, and copper were each referred to, especially to the action of the air of towns and manufacturing districts.

NOTICES OF BOOKS

Thermodynamics and Chemistry. A Non-mathematical Treatise for Chemists and Students of Chemistry. By P. DUHEM. Authorised Translation by GEORGE K. BURGESS. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 8vo. Illustrated. Pp. xxi.—445.

CHEMISTS, especially those engaged in teaching classes in advanced chemistry, will heartily welcome Dr. Burgess's translation of "*Thermodynamique et Chimie*" by the brilliant Professor of Physics at the University of Bordeaux, M. P. Duhem.

In the United States, the author's eulogistic remarks on the work of the late Prof. J. Willard Gibbs will be read with due appreciation. Prof. Duhem writes:—"Many do not hesitate to compare the illustrious author of the *Phase Law* to our Lavoisier." Elsewhere the French chemist writes of Gibbs's work as the natural continuation of Lagrange's "*Mécanique Analytique*," and points out the international character of its subsequent development, for it was transformed into chemical theory first in Holland, by van der Waals, Bakhuis, Roozboom, and van't Hoff, as well as by the labours of Henri Sainte-Claire Deville in France.

In the volume under review the calculus is not used, and the reader is supposed to have no attainments in mathematics and in physics beyond those possessed by the graduate of a good high school.

The first 100 pages deal with the principles of chemical status; after this, the author takes up the phase rule and the philosophy of monovariant and bivariant systems—a classification that he esteems of great utility. Mixed crystals, critical states, the mechanics of perfect gases, chemical dynamics, and explosions, occupy the remainder of the volume.

Three indexes help the reader to find that sought—an index of authors cited, an index of chemical substances studied, and a general index.

In its original language this treatise is already favourably known, in its English dress it deserves a wider acquaintance.

Introduction to the Rarer Elements. By PHILIP E. BROWNING. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. viii.—157. 8vo.

THIS useful work fills a long-felt want, for larger works on general chemistry cannot give the space to the rarer elements which they deserve, nor indeed are details of these rare bodies needed in works having in view merely instruction.

Since there is no table of contents, nor list of elements dealt with, a brief survey of those included may be of interest to those wishing to become acquainted with the scope of this book. It includes the following elements in the order given:—Cs, Rb, Li; Be, Y, and Y earths; Ce, La, Dd, Pr, Nd; Th, Zr, Ge, Ti, Nb, Ta; In, Ga, Tl, V, Mo, W, U; Te, Se; Pt, and associated metals, Au, and the new gases of the atmosphere.

The treatment of each of these is the same; history occurrence, preparation, compounds, characteristics, and experimental work on the group.

The absence of theoretical speculations is shown throughout the work. The author is quite up to date in his methods, but is it not peculiar to find radium alongside of lucium, etherion, and other elements of "unconfirmed discovery"?

A Laboratory Guide to Qualitative Analysis with the Blowpipe. By F. M. MARTIN. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 12mo. Pp. iv.—47.

THIS little book shows how blowpipe reactions may be used to distinguish forty-three of the elements and twenty acids. Being for the use of teachers having a comprehensive knowledge of chemical facts, details which might prove tedious have been omitted, and the entire course of testing is presented in a series of tables occupying only 30 pages. Besides using the blowpipe, many tests are made by the aid of sealed and open glass tubes on a plaster tablet, and with the assistance of several reagents, notably HI, HBr, SnCl_4 , and $\text{Co}(\text{NO}_3)_2$, as well as the more common borax, sodium carbonate, potassium nitrate, &c.

The methods are simple and easily managed, and in skilled hands must be very satisfactory. Some of the tests are very suggestive.

Teachers will do well to give this inexpensive little book a trial. There is an index.

The Praxis of Urinary Analysis. A Guide to the Chemical Analysis of Urine, with Directions for Preparing Artificial Pathological Urine for Practising the Various Tests, and an Appendix on the Analysis of Stomach Contents. By LASSAR-COHN. Authorised Translation from the Author's Enlarged and Revised Second Edition, by H. W. F. LORENZ. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 12mo. Pp. 58.

THE first edition of this useful little book was published in 1897, and it met with such great success that a second edition was called for within six months. This translation by Dr. Lorenz will make it available to those preferring the English language, especially students of medicine. Following the introduction, the book deals with qualitative tests, quantitative methods, the character of normal urine, and, lastly, the analysis of stomach contents. An excellent feature of the book is the presentation of methods excluding ambiguities and convenient of performance. The book can be recommended to those having limited training in chemical analysis.

H. C. B.

International Catalogue of Scientific Literature. First Annual Issue. D. Chemistry, Part II. Published for the International Council by the Royal Society of London. London: Harrison and Sons. Paris: Gautier-Villars. Jena: Gustav Fischer. 1903. Pp. 671.

THE "International Catalogue of Scientific Literature," commencing with the literature of the year 1901, is an outgrowth of the "Catalogue of Scientific Papers" published by the Royal Society of London. The history of its inception and the means adopted to bring the idea to a practical issue has been already given in our columns.

The branches of science to be included in the catalogue are seventeen in number, and the volume now before us is marked D, and deals with Chemistry. A Schedule of Classification and an Index thereto are prefixed to each volume in English, French, German, and Italian; this will not only enable the scientific worker to study the classification in the language with which he is the most familiar, but also in cases of doubt enable him to refer to the corresponding entry in another language. The various headings and sub-headings throughout the Subject Index are given in English; the entries in the Subject Indexes are in the language of the original paper when that is one of the five following languages:—Latin, English, French, German, and Italian, but in cases of translation the name of the original language is given in rounded brackets.

In the Authors' Catalogue each title is given in the original language, subject to the above mentioned restrictions.

After reading the instructions as to the method and marks used in cataloguing, any entry can be found without

much difficulty. We think, however, that it would facilitate matters if "headlines" could be placed at the top of each page, giving some reference as to the subject dealt with on such a page. At the end of the volume there is a list of journals referred to with their abbreviated titles, a short list of errata on page 648, and an index to the subject catalogue.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 13, September 28, 1903.

Compound of Aluminium Sulphate with Sulphuric Acid.—E. Baud.—When bauxite is acted upon by sulphuric acid diluted with its own volume of water, as in the case of the preparation of aluminium sulphate, after a definite time of heating a copious crystalline deposit is formed. This is evidently not ordinary aluminium sulphate, as it is not precipitated by sulphuric acid, and also it only dissolves with difficulty in cold water. If the bauxite is replaced by pure aluminium hydrate the same phenomenon occurs. After purifying and drying, the substance is found to have the composition $\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 4\text{H}_2\text{O}$. It dissolves very slowly in cold water, but more rapidly in hot. The formation of this compound is probably the result of three concurrent phenomena: partial dehydration of the aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, combination with sulphuric acid, and molecular modification.

Nitrosite of Pulegone.—P. Genvresse.—The nitrosites of the cyclicketones possessing one or several double liaisons have up to the present time never been prepared. The author experiments on carvone and pulegone. In the case of carvone the experiments were unsuccessful, but pulegone nitrosite, $\text{C}_{10}\text{H}_{16}\text{ON}_2\text{O}_3$, can be obtained by two methods—from amidon and nitric acid either with nitrogen peroxide or with nitrous vapours.

Preparation of Sulphuretted Hydrogen from Organic Extracts and Albumenoid Matter in general.—E. Pozzi-Escot.—When an extract is made of residues from a brewery by the method described in a former paper, and this extract is mixed with flowers of sulphur, a large quantity of sulphuretted hydrogen is evolved at ordinary temperatures. The same extract treated with chloroform, but not with sulphur, gives off no sulphuretted hydrogen in twelve hours at ordinary temperatures. If, however, this latter extract is boiled for three minutes, and, after cooling, chloroform and flowers of sulphur are added, no evolution of gas takes place. The aqueous extract of the residue, if brought to boiling-point in presence of sulphur, immediately gives forth a copious evolution of sulphuretted hydrogen when hot, but, on cooling, and the vessel being absolutely freed of all trace of this gas by agitation with carbon dioxide and left for twelve hours at the laboratory temperature, no further evolution of sulphuretted hydrogen can be obtained. On the other hand, if the aqueous extract is left in presence of sodium bisulphite, at the end of a definite time a considerable quantity of sulphuretted hydrogen is evolved. From these experiments and certain others, it appears reasonable to conclude that the production of sulphuretted hydrogen, in abundance and without limit, by organic extracts, and in particular by extracts of brewing residues, is due to a phenomenon of a diastasic nature.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 8.

A New Class of Peruranates.—J. Aloy.—Already inserted in full,

Quantitative and Qualitative Analysis of Cobalt Compounds.—H. Copaux.—Already inserted in full.

Oxidation by means of Chromic Acid in the presence of other Acids.—Maurice Prud'homme.—To obtain a white design on a background of indigo the tissue is printed with a colour containing chromate of potash or soda. It is then passed through a bath heated to 50°, generally containing 50 grms. of oxalic acid and 50 grms. of sulphuric acid; the tissue is left in for half a minute or a minute. During this time, the liberated chromic acid must oxidise and destroy the indigo. Experiments made by the author with a mixture of chromic and oxalic acids have shown that:—When the chromic acid remains constant, the speed of oxidation of the indigo varies proportionally to the amount of oxalic acid. When the weights of the chromic and oxalic acids vary, but retain constant proportion one to the other, the speed of the oxidation varies according to the square of the weight of the oxalic acid; the speed of oxidation is also proportional to the product of the masses of the chromic and oxalic acids present. By using sulphuric acid instead of oxalic acid, analogous results were obtained. This fact is the more remarkable since sulphuric acid is not a reducing agent like oxalic acid, to which a certain facility of starting the oxidation by means of chromic acid has been attributed, on account of its reducing properties. The result of the research is the finding of the following general rule:—The speed of the reduction of chromic acid by oxalic acid is proportional to the weight of the chromic acid and to the number of molecules of oxalic acid, which exceeds 3, and inversely proportional to the dilution.

Action of Metals at a High Temperature on the Fatty Acids.—Alexandre Hébert.—Already noticed.

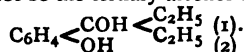
On the Mechanism of the Action of Zinc Powder at a High Temperature on the Fatty Acids.—Alexandre Hébert.—The action of zinc powder at a high temperature on the lower fatty acids gives rise to fairly simple carbides, which are related more or less directly to the original acid; but as soon as we rise in the series, and take, for instance, the C₁₂, and even to a greater extent with the C₁₈ groups, there is at the same time as the reaction a more or less complex and profound polymerisation, producing ethylenic carbides of high molecular weights, and which cannot be connected, at any rate in a simple manner, with the fatty acids from which they have sprung.

Essence of Roman Camomile. Preparation of Angelic Acid. Preparation of Tiglic Acid.—E. E. Blaise.—To effect the synthesis of the α,β-dimethylglutaric acids, the author turned to the condensation of the angelic and tiglic ethers by means of cyanacetate of ethyl soda, but he had to prepare first the angelic and tiglic acids. As angelic acid could not be obtained synthetically, it was extracted from essence of Roman camomile by saponification; 500 grms. of the essence gave 65 grms. of re-crystallised angelic acid. To prepare tiglic acid, the author had recourse to the dehydration of α-methyl-β-oxybutyric acid; the ether corresponding to this acid was prepared by condensing ordinary aldehyde and α-bromopropionic ether in the presence of zinc. 150 grms. of α-methyl-β-oxybutyric ether were poured gradually on to 225 grms. of perchloride of phosphorus. The action was terminated by heating for half-an-hour on a water-bath, then decomposing by means of water. The raw product thus obtained contains about 33 per cent of tiglate of ethyl and 66 per cent of β-chloridised ether. It is saponified directly with alcoholic potash, which at the same time transforms the chloridised ether into tiglic acid. After the elimination of the alcohol, the acid recovered from the alkaline salt consists of almost pure tiglic acid, which crystallises rapidly. The transformation of angelic and tiglic acids into ethylenic ethers is effected very easily by heating these acids on the water-bath for six hours with one and a-half times the theoretical quantity of absolute alcohol treated with 15 per cent of sulphuric acid.

Isopyromucic Acid.—G. Chavanne.—Already noticed.

A New Product of the Reduction of Dinitrostilbene-disulphonic Acid: Nitroamidostilbene-disulphonic Acid.—A. Wahl.—One hundred grms. of dinitrostilbene-sulphonate of sodium were dissolved in 1000 c.c. of warm water and cooled down to 30–40°. We then add slowly a solution of 70 grms. of crystallised sulphide of sodium in 400 c.c. of water. The addition of the sulphide causes a slight rise of temperature, which is checked by placing the flask in cold water. After about a quarter of an hour, all the soda salt of the dinitrostilbene-disulphonic acid has disappeared; acidulate with 100 c.c. of concentrated hydrochloric acid. An abundant yellow crystalline precipitate is formed, which, after complete cooling, is drained and washed with salt water. This product can be purified by dissolving it in carbonate of sodium and precipitating the filtered solution with hydrochloric acid. To obtain it perfectly pure, it is dissolved in boiling water, acidulated with acetic acid, and left to crystallise by cooling. The analysis of this product, dried at 130–150°, corresponds to the formula C₁₄H₁₁N₂O₈S₂ · Na; that is to say, an acid sodium salt of nitro-amido-stilbenedisulphonic acid.

Diethylorthoxyphenylcarbinol and its Derivatives.—A. Mounié.—The author has examined the products of the reaction of bromide of ethyl-magnesium on salicylate of methyl, to verify, in particular, whether the first isolable product would not be the tertiary alcohol expected,—



He easily attained his object; the tertiary alcohol thus obtained is the diethylorthoxyphenylcarbinol, which is a perfectly stable crystalline body under ordinary conditions, but which decomposes when distilled *in vacuo*.

MISCELLANEOUS.

Conditions which Determine the Sign and the Magnitude of Electrification by Contact.—Jean Perrin.—Electric osmosis affords an easy method of investigating the charge due to contact of any solid and any liquid. The charge produced is larger in proportion as the body is capable of easy ionisation, such as water. The electrification is, in fact, due to the ions present in the liquid. The only ions which are directly active in water are H⁺ and OH⁻. Each of these takes a charge corresponding to its sign. All polyvalent positive ions diminish the action of the OH⁻ ions present, and all polyvalent negative ions that of the H⁺ ions. This paralyzing action increases with the concentration and with the valency.—*Comptes Rendus*, cxxxvi., No. 14.

Casting Copper in Sand.—(*Metal Industry*).—If the copper has overheated, it often explodes as it sets, and no good castings are produced. If it is cast without being overheated, liquid copper oozes from the gate for some time during setting, while the casting is full of blow-holes, caused by carbonic oxide. Phosphorus can absorb the oxygen present in the metal as cuprous oxide, but not that as carbonic oxide. Silicon can do both. One pound of silicon-copper containing 10 per cent of silicon is added to 100 pounds of copper, introducing 0.1 per cent of silicon. This amount suffices, if the copper is kept well covered with charcoal and not overheated. A plumbago stirrer is used for mixing the bath, and time is given for the silica formed to rise to the surface. The metal is then skimmed and poured. The silicon may be doubled, if high electrical conductivity of the castings is not a prime desideratum. The precautions to take are summarised as:—1. Use a clean crucible and keep it for this work. 2. Use graphite stirrers and skimmers; iron is rapidly attacked by silicon. 3. Keep metal well covered with charcoal. 4. Do not overheat. 5. Stir, and give time for silica to rise. 6. Cast pattern with finished side down, avoiding blow-holes in it, which rise to the upper surface. 7. Do not pour too cold. 8. Silicon will not make up for carelessness in handling the metal.—*Journ. Am. Chem. Soc.*, xxv., No. 5.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nitrogen-fixing Bacteria.—I should feel very much obliged if you could give me the address of a laboratory where I can obtain "Alinit," the nitrogen-fixing bacteria for applying to land to increase its fertility. I am anxious to obtain a phial of this for experimental purposes, and will feel very grateful if any of your correspondents can oblige me. Can you also give me any useful and late publications referring to atmospheric nitrogen-fixing bacteria?—HOWARD B. EVANS.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting. Geological, 8.

Society of Chemical Industry, 8. "On the Application of the X Rays to the Examination of 'Safety Fuses,'" by C. Napier Hake, Chief Inspector of Explosives, Melbourne, Australia (to be read by Prof. W. R. Hodgkinson). "Scarlet Phosphorus—A New Chemically Active Variety of Red Phosphorus, and its Use in the Manufacture of Matches," by Drs. Marquart and Schulz (to be read by W. Muir). "New Compound of Phosphorus for the Production of Matches" by F. Bale. "Densities of Concentrated Nitric Acid at Different Temperatures," by Prof. V. H. Veley, F.R.S., and J. J. Manley. "On a Comparison of different Types of Calorimeters," by J. S. S. Brame and Wallace A. Cowan.

THURSDAY, 5th.—Chemical, 8. "Conductivity of Substances Dissolved in certain Liquefied Gases," by B. D. Steele and D. McIntosh. "The Reduction of Hydrazoic Acid," by W. T. Cooke. "The Behaviour of Metallic Oxides towards Fused Boric Anhydride," by C. H. Burgess and A. Holt, jun. "Some Reactions of Vanadium Tetrachloride," by B. D. Steele. "Studies on Comparative Cryoscopy—Part I, The Fatty Acids and their Derivatives in Phenol Solution," by F. W. Robertson. "The Vapour-pressure of Sulphuric Acid Solutions," by B. C. Burt. "The Viscosity of Liquid Mixtures," by A. E. Dunstan and W. H. C. Jemmett. "Additive Compounds of *s*-Trinitrobenzene and Alkylated Arylamines," by H. Hibbert and J. J. Sudborough. "A Contribution to the Study of the Reactions of Hydrogen Peroxide," by J. McLachlan. "The Constitution of certain Silicates," by C. Simmonds. "Constitution of Ethyl Cyanacetate, Condensation of Ethyl Cyanacetate with its Enolic Form," F. Remfry and J. F. Thorpe. "Interaction between Chloric and Hydroiodic Acids," by J. McCrae. "3, 5, Dichloro-1 : 1 : 2-trimethyldihydrobenzene (a Correction)," by A. W. Crossley. "The Estimation of Hydroxylamine," by H. O. Jones and F. W. Carpenter. "A Study of the Isomerism and Optical Activity of Quinquevalent Nitrogen Compounds," by H. O. Jones. "The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic," by W. T. Cooke. "The Union of Carbon Monoxide and Oxygen, and the Drying of Gases by Cooling," by A. F. Girvan.

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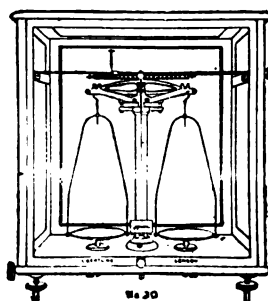
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By M^{me}. SKŁODOWSKA CURIE.

(Continued from p. 212).

CHAPTER III. (continued).

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Under some circumstances there is a production of ozone in the neighbourhood of very active compounds. Rays emerging from a sealed jar containing radium do not produce ozone in the air they pass through. On the contrary,

a strong odour of ozone is detected when the jar is opened. In a general way, ozone is produced in the air when the latter is in direct contact with the radium. Communication by a channel, even if extremely narrow, suffices; it appears as if the production of ozone is associated with the propagation of induced radio-activity, of which we shall speak later.

Radium compounds appear to change with lapse of time, doubtless under the action of their own radiation. It was seen above that crystals of barium-radium chloride, which are colourless when formed, become gradually coloured first yellow or orange, then pink; this colouration disappears in solution. Barium-radium chloride generates oxygen compounds of chlorine; the bromide those of bromine. These slow changes generally manifest themselves some time after the preparation of the solid product, which at the same time changes in form and colour, becoming yellow or violet. The light emitted also becomes more violet.

A solution of a radium salt evolves hydrogen (Giesel).

Pure radium salts seem to undergo the same changes as those containing barium. However, crystals of the chloride, deposited in acid solution, do not become sensibly coloured after some time has elapsed, whereas crystals of barium-radium chloride, rich in radium, become deeply coloured.

Production of Thermo-luminescence.—Certain bodies, such as fluorite, become luminous when heated; they are thermo-luminescent. Their luminosity disappears after some time, but the capacity of becoming luminous afresh through heat is restored to them by the action of a spark, and also by the action of radium. Radium can thus restore to these bodies their thermo-luminescent property. Fluorite when heated undergoes a change, which is accompanied by the emission of light. If the fluorite is afterwards subjected to the action of radium, an inverse change occurs, which is also accompanied by an emission of light.

An absolutely similar phenomenon occurs when glass is exposed to radium rays. Here also, a change is produced in the glass while luminous from the effect of the radium rays; this change shows itself in the colouration which appears and gradually increases. If the glass is afterwards heated, the inverse change takes place, the colour disappears, and this phenomenon is accompanied by production of light. It appears very probable that we have here a change of a chemical nature, and the production of light is associated with this change. This phenomenon may be general. It might be that the production of fluorescence by the action of radium and the luminosity of radium compounds is of necessity associated with some chemical or physical change in the substance emitting the light.

Radiographs.—The radiographic action of the new radio-active bodies is very marked. However, the method of operating should be very different with polonium and radium. Polonium acts only at very short distances, and its action is considerably weakened by solid screens; it is practically annihilated by means of a screen of slight thickness (1 m.m. of glass). Radium acts at considerably greater distances. The radiographic action of radium rays may be observed at more than 2 m. distance in air, even when the active product is enclosed in a glass vessel. The rays acting under these conditions belong to the β - and γ -groups. Owing to the differences in transparency of different materials to the rays, radiographs of different objects may be obtained, as in the case of Röntgen rays. Metals are, as a rule, opaque, with the exception of aluminium, which is very transparent. There is no noteworthy difference of transparency between flesh and bone. The operation may be carried on at a great distance and with a source of very small dimensions; and very delicate radiographs are thus produced. The beauty of the radiograph is enhanced by deflecting to one side the β -rays, by means of a magnetic field, and utilising only the γ rays. The β -rays, in traversing the object to be radiographed, undergo a certain amount of diffusion, and thus cause a

* Thesis presented to the Faculté des Sciences de Paris.

slight fog. In suppressing them, a longer time of exposure is necessary, but better results are obtained. The radiograph of an object, such as a purse, requires one day with a radiating source composed of several centigrams of a radium salt, enclosed in a glass vessel, and placed at a distance of 1 m. from the sensitive plate, in front of which the object is placed. If the source is at a distance of 20 c.m. from the plate, the same result is obtained in one hour. In the immediate vicinity of the source of radiation, a sensitive plate is instantaneously acted upon.

Physiological Effects.

Radium rays exert an action upon the epidermis. This has been observed by M. Walkhoff and confirmed by M. Giesel, since also by MM. Becquerel and Curie.

If a celluloid or thin indiarubber capsule containing a very active salt of radium be placed upon the skin, and be left thus for some time, a redness is produced upon the skin, either immediately or at the end of some time, which is longer in proportion as the action is weaker; this red spot appears in the place which has been exposed to the action; the local change in the skin appears and acts like a burn. In certain cases a blister is formed. If the exposure was of long duration, an ulceration is produced which is long in healing. In one experiment, M. Curie caused a relatively weak radio-active product to act upon his arm for ten hours. The redness appeared immediately, and later a wound was caused which took four months to heal. The epidermis was locally destroyed, and formed again slowly and with difficulty, leaving a very marked scar. A radium burn with half-an-hour's exposure appeared after fifteen days, formed a blister and healed in fifteen days. Another burn, caused by an exposure of only eight minutes, occasioned a red spot which appeared two months after, its effect being quite insignificant.

The action of radium upon the skin can take place across metal screens, but with weakened effect.

The action of radium upon the skin has been investigated by Dr. Daulos, at the Hospital of St. Louis, as a process of treating certain affections of the skin, similar to the treatment with the Röntgen rays or the ultra-violet rays. In this respect radium gives encouraging results; the epidermis partially destroyed by the action of the radium is renewed in a healthy condition. The action of radium is more penetrating than that of light, and its use is easier than that of light or of Röntgen rays. The study of the conditions of application is of necessity rather lengthy, because the effect of the application does not at once appear.

M. Giesel has observed the action of radium upon plant leaves. The leaves thus treated turn yellow and wither away.

M. Giesel has also discovered the action of radium rays upon the eye. If a radio-active substance be placed in the dark in the vicinity of the closed eye or of the temple, a sensation of light fills the eye. This phenomenon has been studied by MM. Himstedt and Nagel. These physicists have demonstrated that the centre of the eye is rendered fluorescent by the action of radium, and this explains the sensation of light experienced. Blind people whose retina is intact are sensitive to the action of radium, whilst those whose retina is diseased do not experience any sensation of luminosity.

Radium rays either arrest or hinder the development of colonies of microbes, but this action is not very intense.

M. Danyasz has recently demonstrated the ready action of radium upon the marrow and brain. After one hour's exposure paralysis of the animals experimented upon occurred, and the latter usually died in a few days.

Influence of Temperature upon Radiation.

There is so far but little information regarding the manner of variation of the radiation of radio-active bodies with temperature. We know, however, that radiation subsists at low temperatures. M. Curie placed a glass tube containing barium-radium chloride in liquid air. The luminosity of the radio-active body persisted under these

conditions. At the moment, indeed, of removing the tube from the cold bath, it appears more luminous than at the ordinary temperature. At the temperature of liquid air radium continues to cause fluorescence in the sulphates of uranium and potassium. M. Curie has verified, by electrical determinations, that the radiation, measured at a certain distance from the source, possesses the same intensity whether the radium be at the temperature of the atmosphere or of liquid air. In these experiments the radium was placed at the bottom of a tube closed at one end. The rays emerged from the tube at the open end, traversed a certain space in the air, and were received into a condenser. The action of the rays upon the air of the condenser was determined both on leaving the tube in the air and on surrounding it to a certain height with liquid air. The same result was obtained in both cases.

The radio-activity of radium persists at high temperatures. Barium-radium chloride after being fused (towards 800°) is radio-active and luminous. However, prolonged heating at a high temperature has the effect of temporarily lowering the radio-activity of the body. This decrease is very considerable; it may constitute 75 per cent of the total radiation. The decrease is less in proportion for the absorbable rays than for the penetrating rays, which are to some extent suppressed by heating. In time the radiation of the product regains the intensity and composition that it possessed before heating; this occurs after the lapse of about two months from the occasion of heating.

(To be continued).

ON THE RADIO-ACTIVE CONSTITUENT OF THE BISMUTH FROM JOACHIMSTHAL PITCHBLEND.

III.*

By W. MARCKWALD.

I. On Radio-tellurium.

In earlier communications I had shown that from the hydrochloric acid solution of the radio-active bismuth chloride, as it is obtained from Joachimsthal pitchblende, the radio-active constituent can be separated from the bismuth in two ways. On immersing metallic bismuth or antimony in the solution, the active constituent, mixed with various other substances is deposited on the metal, and by tin chloride it is precipitated in a purer condition as a fine black precipitate. On account of the complete agreement of the last product with tellurium in all its properties—with the exception of radio-activity—I had provisionally called it radio-tellurium.

By using 6 kilogrms. of bismuth oxychloride, which resulted from about 2000 kilogrms. of pitchblende, I have obtained 1.5 gm. of this radio-tellurium. Further examination showed that it consists almost entirely of ordinary tellurium, so that the radio-active constituent certainly amounts to only fractions of 1 per cent. For the separation of the tellurium the metal was converted into the chloride, and the tellurium was precipitated from a hydrochloric acid solution of moderate strength by means of hydrazine chloride (A. Gutbier, *Berichte*, 1901, xxxiv., 2724). It is then still decidedly active, but in order to obtain almost inactive tellurium it is sufficient to repeat the precipitation once.

The filtrate contains the active substance still adulterated with bismuth, tin, and some tellurium. If some drops of a solution of tin chloride are added to the solution after it has been concentrated, on digesting on the water-bath a very small quantity of dark precipitate separates, and may be collected on the filter. Its weight amounted to 4 milligrams. I am not by any means convinced that this product is now a single substance. But in view of the great costliness of

* Cf. *Berichte*, 1902, xxxv., 2285 and 4239; see also *Chemiker. Ztg.*, 1902, xxvi., 895.

the material, I have decided that for the present I must abstain from a further chemical examination until I am able to procure greater quantities.

The filtrate from the tin chloride precipitation still contains small quantities of the active substance, even if the filtration is repeated many times, conceivably in colloid solution. The following observations confirm this view:—If to one part of the filtrate some tenths of a milligram of tellurous acid in aqueous solution are added, the tellurium precipitation resulting from the excess of tin chloride completely brings down the active substance. If in another part of the filtrate a stick of bismuth is immersed, it becomes only feebly active after longer action; but if some drops of bromine water are previously added in order to oxidise the tin chloride and to convert any colloidal dissolved metal into bromide, the active substance is completely precipitated on the metal rod, and it becomes exceedingly active. This phenomenon is of the greatest value, if it is desired to separate the active substance from a solution which contains much bismuth, but no tellurium. This will be further discussed hereafter.

The active substance is readily soluble in cold dilute nitric acid. On driving off the acid and taking up the residue with hydrochloric acid, the solution of the chloride is obtained, from which, by the immersion of metallic plates of copper, tin, antimony, &c., the active substance may be precipitated in a very finely divided state. In order to give some idea of the activity of such precipitates, it may be stated that on a copper plate of 4 sq. c.m. surface a precipitate of about 10^{-10} m.grm. is sufficient to make the illumination of a zinc blende screen which is brought close to the plate visible to an audience of many hundred people.

If this substance is contained in pitchblende in much smaller quantities than radium, its separation, on the other hand, when once a suitable method has been found, presents only trifling difficulties, because chemical reactions may be employed for this purpose, which is at present not the case in the separation of radium from barium.

I am indebted to the Royal Academy of Science at Berlin for the costly material which was used in this research.

II. On Polonium.

My last article has been followed by many publications under the above title, the purport of which I must shortly discuss. M^{me}. S. Curie (*Physikal. Zeit.*, iv., 234) guards against her incidental observation, "polonium is only a species of active bismuth," being taken to mean that she had given up seeking a new element in polonium, and communicates some reactions, recently observed by her, which the polonium enriched by her fractionation method and differing from bismuth exhibits. As regards the first point, it is quite superfluous to emphasise the fact that I had not the least intention of belittling the great and lasting reputation which the Curies have earned by the discovery of the new radio-active elements, when I quoted that sentence.

The new observations of M^{me}. Curie on the properties of her enriched polonium confirm the idea, already entertained by me, that this substance is by no means identical with radio-tellurium. Polonium gives on precipitation of the nitric acid solution with water precipitates which are insoluble in acids, and of a white or yellow or brown colour, a striking difference from radio-tellurium and one which is of far greater importance than the inconstancy of the radiating power of polonium. Whether the Curies' polonium does not perhaps also contain some of the radio-tellurium is a question the examination of which must be left to the discoverers of polonium.

Two articles on this subject by F. Giesel have recently appeared. The first (*Berichte*, 1903, xxxvi., 728) essentially confirms my earlier observations, as far as they relate to the production of a radio-active precipitate on a little stick of bismuth.

In a footnote the author alludes to the fact that platinum, gold, and palladium also become radio-active to a lesser degree on immersion in the polonium solution, but leaves

it an open question whether the reactions which occur are analogous to those which take place in the case of bismuth. That this phenomenon, already observed by me in the case of platinum, which, moreover, is also exhibited by tellurium, is due to quite other causes, follows from the fact that all these metals after remaining for a longer time in contact with the solution do not appreciably diminish the activity of the dissolved substance, while bismuth entirely separates the substance which carries the activity from the solution.

Giesel has not been able to prove the presence of tellurium in the polonium, and did not get the tin chloride reaction. This want of success depends only on the lack of tellurium. I have obtained "polonium" from the Chininfabrik Braunschweig, which Giesel manages. A grm. of the oxychloride was dissolved in hydrochloric acid, and a drop of tin chloride solution added. Even after lengthy digestion no visible precipitate appeared, but when the solution was filtered a perceptible brown colouration could be seen on the filter. After washing, the filter was radio-active to the highest degree, and was quite equivalent to my strongest preparation. The filter smelt strongly of ozone, and was completely destroyed in the course of some weeks. As described above, a trace of tellurous acid was added to the filtrate in order to bring down the rest of the radio-active substance. The bismuth now separated from the solution showed only feeble α -radiation, but the γ -radiation was not much diminished.

In his article "On Polonium and the Inducing Character of Radium" (*Berichte*, 1903, xxxvi., 2368), which has just appeared, Giesel communicates an observation which seems to him to be capable of putting a new aspect on the polonium question. By immersing a little piece of bismuth in radium bromide solution he obtained strongly α -radiating metal; owing to the fact that Giesel associated this observation with mine, the impression was produced that the activity might have the same cause in both cases. However, this is by no means the case.

The experiment described by Giesel was planned by me some time ago. I certainly did not possess nearly such strong radium preparations as Giesel. But even using a preparation containing about 1 per cent of radium, a little rod of bismuth immersed in it assumes strong activity. The strength of the radiation is, to be sure, not to be compared with that of my strongest radio-tellurium. This phenomenon is clearly completely analogous to the above described which Giesel and I have observed when the noble metals are immersed in polonium solutions. In both cases the active constituent was not appreciably, much less completely, withdrawn from the solution.

However, Giesel's newest communication led me to arrange another experiment, which was quickly carried out, and tended to confirm my views of the matter. 0.01 grm. of radium chloride (of about 2.5 per cent) was mixed with 0.2 m.grm. of tellurous acid in weak hydrochloric acid solution and the tellurium precipitated with tin chloride. As was to be expected the tellurium precipitated was strongly active. But in spite of the most thorough washing all precipitates from a solution containing radium are more or less active. But when the metal was dissolved off the filter with nitric acid, converted into the chloride, and precipitated from a very dilute solution on copper, the activity was scarcely capable of detection by the electroscope. Thus the tellurium rendered active by induction (?) behaves quite differently from the radio-tellurium.

Finally, I must shortly discuss a sentence in Giesel's article in order that it may not be thought that I agree with it. Giesel writes:—

"Marckwald considers that the precipitate formed on the bismuth consists, at any rate in part, of metallic polonium, and regards the electrolytic separation as the proof of the existence of an (electro-negative) element, differing from bismuth, and allied to tellurium."

In an earlier article I have emphasised to Giesel the fact that I do not lay claim to the name polonium for the radio-active substance separated by me. The idea called forth by this name is so indefinite, from the fact that it was used

when radio-active bismuth was discovered, that it is now necessary to distinguish between the Curies' and Giesel's polonium. It would be a mistake to call a third substance polonium. Hence for the present I have called the substance separated by me "radio-tellurium." By this I do not wish it to be understood that I regard its close connection with tellurium as *proved*. On all occasions I have emphasised the fact that this connection was only *conjectured* by me. This conjecture has been of much use to me, because it has suggested to me the method for the separation of the active substance; for its separation not only from bismuth, but also from tellurium. However, I am far from wishing to draw from this fact any decisive conclusions about the nature of a substance which I believe has not yet been obtained in a pure state.—*Berichte der Deutsch. Chem. Gesell.*, 1903, xxxvi., 2662).

ON RADIO-ACTIVE THORIUM.

By K. A. HOFMANN and F. ZERBAN.

WE have already alluded to the fact that freshly-made thorium preparations are strongly radio-active to different degrees, according to the amount of uranium contained in the minerals (*Berichte*, 1902, xxxv., 531). More recent experiments have confirmed this conclusion, as shown in the accompanying table.

It may here be noted that the preparations marked "very feebly active" produced a decided effect on the photographic plate through black paper only after an exposure of twenty hours, while the "feebly active" almost equalled uranic-uranous oxide in photographic and ionising effect. The effect of the "very strongly active" was nine to ten times greater, and this activity could be made still greater by various methods. But after one and a-half to two years all these preparations exhibited nearly uniformly only very slight penetrating β -activity, while the ionising α -radiation fell to very nearly the value of that of the uranium preparations, and after that could hardly be further diminished. This residual activity cannot be removed even by ignition for one hundred hours (as a gas-mantle, for example), nor even by the enormous heat of reduction with magnesium in a current of hydrogen, as our latest experiments have shown. Also, on mixing the chloride with fifty times its quantity of barium chloride in solution and precipitating the barium with sulphuric acid (after standing for eight days), the activity could not be completely removed from the thorium earth from euxenite.

It might be supposed that this residual effect was due to a trace of actinium (*cf.* below); but the thorium preparations made artificially active by uranium behaved so like those obtained from the uranium minerals as regards the passing away of the activity (Hofmann and Zerban, *Berichte*, 1902, xxxv., 533) that it must at least be concluded that the original strength of the thorium activity depends upon induction by means of the uranium present in most thorium minerals.

The question whether pure thorium and its compounds possess in themselves primary radio-activity may be answered in the negative, as inactive thorium earth was obtained from orthite from Fredenstrandsrand (which was quite free from uranium)*, ytrotitanite and gadolinite (Sotersdalen in Norway). In order to show that these were undoubtedly thorium earths, 4 kilogrms. of gadolinite from Sotersdalen were prepared in the usual way, and the oxalate precipitate extracted with ammonium oxalate (*cf.* Jannasch, "Leitfaden der Gewichtsanalyse"). The thorium oxalate separated from the filtrate by acidulating was ignited, and the earth repeatedly precipitated with hydrogen peroxide, and with sodium thiosulphate to ensure perfect purification.

* In minerals containing phosphoric acid the proof of the presence of uranium is best established by Laube's method (*Zeit. f. Angew. Chem.*, 1889, 475).

0.0776 grm. of the sulphate of constant weight at 360° gave, after strong ignition, 0.0482 grm. of oxide, which corresponds to an equivalent weight of 57.21 ($H = 1$) or 57.63 ($O = 16$), while for pure thorium the accepted values are 57.7 ($H = 1$) or 58.1 ($O = 16$).

We found that the specific gravity of the oxide was 9.112 at 20°; according to Chydenius and Damour the specific gravity of the pure thorium earth varies from 9.21 to 9.366.

Thus the results we obtained agree sufficiently with those established by other investigators to prove that the oxide isolated by us, though only in small quantities, from gadolinite (Sotersdalen) was identical with thorium earth.

It was quite without effect on the photographic plate after an exposure of twenty-four hours through thin black paper, and did not appreciably accelerate, even with varying arrangement, the discharge of a very sensitive Elster-Geitel electroscope. Generally speaking, if even a trace of activity was present, its amount would have to be estimated at 1/7th of the strength of an Auer-mantle prepared from monazite sand, and ignited for about 100 hours, as accurate experiments showed.

It was interesting to notice that the gadolinite from which this inactive thorium earth was derived exhibited the property of suddenly glowing throughout the whole mass on heating, and in greater quantities with such violence that a part of the powder was scattered like dust. No gases were evolved, but only water vapour.

2.286 grms. of gadolinite gave 0.0090 grm. of water (weighed in a calcium chloride tube), with a loss of weight of 0.0088 grm. Thus, calculated to 100 parts of the mineral, the loss of water is 0.394 per cent. Of this, 0.309 per cent of water escapes below, and 0.085 per cent of water escapes at the temperature of glowing, which was found to be about 430°. As the greater part of the water evaporates below this temperature the illumination occurring with development of heat depends, not on the dehydrating of the mineral, but on an exothermic change.

That this pyroluminescence of gadolinite from Sotersdalen is not connected with the radio-activity follows from the fact that neither the mineral itself nor its constituents, especially the thorium earth, had any effect whatever on the photographic plate or the electroscope.

While the thorium earth from the minerals mentioned above by induction with uranium is given an only temporary activity, which is sometimes considerable, the small quantities of a substance similar to thorium obtained from pitchblende, Debierne's actinium (*Comptes Rendus*, 1900, cxxix., 593, and cxxx., 906) remain very strongly active for a year. We proceeded to the treatment of the soda precipitates, to be obtained commercially, of the uranium nitrate mother-liquor, and heated the part belonging to the ammonium sulphide group as chloride with excess of sodium thiosulphate. The precipitate was extracted with hot dilute sulphuric acid, the residue ignited, and fused with potassium carbonate. The part thus obtained, which was insoluble in water and in hydrochloric acid, was evaporated with sulphuric acid, dissolved in ice-water, and the nearly neutral filtrate was precipitated with oxalic acid. The earth obtained from the oxalate was yellowish-white, and approximately showed the reactions of the thorium earth, *i.e.*, it was precipitated by thiosulphate when heated and by hydrogen peroxide, and also by oxalic acid from feebly acid solution. Also on treating the oxalate with warm ammonium oxalate solution it dissolved like thorium, but unlike the latter could not be precipitated from the filtrate either by ammonia nor by acids, but remained behind after evaporation and ignition of the dissolved portion. The solubility of the dry sulphate in ice-water, which was small in comparison with that of thorium, was noteworthy, and also the rapidity with which the ignited oxide dissolved in concentrated sulphuric acid.

This "actinium" (in Debierne's sense) differs from Giesel's emanation substance (*Berichte*, 1903, xxvii., 344) in that it may be precipitated by means of thiosulphate, and is soluble in ammonium oxalate.

Mineral.	Amount of U ₃ O ₈ contained in it.	Amount of ThO ₂ contained in it.	Activity of the thorium earth immediately after precipitation.
Bröggerite	About 78 per cent (a)	About 15 per cent (a)	Very strongly active.
Cleveite	70 per cent on an average (b)	7 per cent on an average (b)	Very strongly active.
Euxenite	5—12 per cent (c)	Very small	Strongly active.
Samaraskite	4—17 per cent (d)	About 4 per cent (d)	Strongly active.
Fergusonite	1·5—7 per cent (e)	1—3 per cent (e)	Feebly active.
Xenotime	0·5—3½ per cent (f)	0·5—3·5 per cent (f)	Feebly active.
Thorite	About 10 per cent (g)	About 50 per cent (g)	Feebly active.
Orangite	About 1 per cent (g)	About 72 per cent (g)	Very feebly active.
Æschynite	0·31 per cent (h)	About 16 per cent (h)	Very feebly active.
Monazite sand	About 0·1 per cent (i)	1—2·5 per cent (j)	Very feebly active.

- (a) K. A. Hofmann and W. Heidepriem, *Berichte*, 1901, xxxiv., 914.
 (b) Rammelsberg, "Handbuch der Mineralchemie," 2 Suppl., 2nd edition, p. 67.
 (c) Herzfeld and Korn, "Chemie d. Selt. Erden," p. 10.
 (d) Rammelsberg, *loc. cit.*, p. 167.

- (e) *Ibid.*, p. 166.
 (f) *Ibid.*, p. 138.
 (g) Herzfeld and Korn, *loc. cit.*, p. 28.
 (h) *Ibid.*, p. 39.
 (i) *Ibid.*, p. 40.
 (j) *Ibid.*, p. 37.

The ionising radiation of the purest preparations was 1500 times greater than that of uranic-uranous oxide, while the action penetrating 4 c.m. of air and aluminium foil ½ m.m. thick is only ten times greater than that of uranium. The phosphorescence produced on Sidot's blende was clearly visible, but the emanation was only small, and was shown by the electroscope only for about two minutes after the removal of the preparation.

Since the examination of actinium by spectrum analysis has as yet provided no certain proof of the existence of an element differing from thorium, an equivalent weight determination was carried out, using a preparation which had been purified by precipitation with ammonia, oxalic acid, and, finally, with hydrogen peroxide. 0·0306 gm. of sulphate of constant weight at 360° gave 0·0196 gm. of oxide. This corresponds to an equivalent weight of 62·87 (H = 1) or 63·32 (O = 16), while for pure thorium the values are 57·7 (H = 1) or 58·1 (O = 16).

In spite of this difference, and of the quantitative peculiarities mentioned above, it is still doubtful whether the elementary nature of actinium is really different from that of thorium, for it is possible that by very strong induction of radio-activity the chemical properties of an elementary atom may be modified. To what extent this is possible shall next be thoroughly examined.

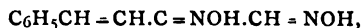
The circumstance that the activity of the actinium preparations has not diminished in a year would not in itself be a proof that the thorium earth from pitchblende contains a primarily active element (actinium), for Hofmann and Wölfl's (*Berichte*, 1903, xxxvi., 1040) pieces of silver and palladium made active by radio-lead chloride solution have retained their ionising power up to the present (for six months). But the fact that the activity of the thorium earth from bröggerite, cleveite, euxenite, and samarskite, as well as of that made active by uranium diminished very decidedly in some months, while the small quantities of a substance similar to thorium from pitchblende did not diminish in strength in a year, argues in favour of the assumption of a primarily active actinium.—*Berichte der Deutsch. Chem. Gesell.*, 1903, xxxvi., 3093.

THE ACTION OF OXIDES OF NITROGEN ON OXIMIDO COMPOUNDS.*

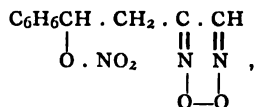
By W. SLOAN MILLS, M.A., Queen's College, Galway,
1851 Exhibition Scholar.

In connection with the study of the chemistry of india-rubber, in which Professor Harries, of the University of Berlin, is at present engaged, and which takes the form in the first place of an investigation into its behaviour towards

oxides of nitrogen, I was entrusted with the simpler preparatory problem to investigate the action of oxides of nitrogen on oximido compounds. For this purpose benzalisonitrosoacetone was prepared, which, on being treated with free hydroxylamine under certain conditions in methyl alcohol solution, yielded long colourless prism-shaped crystals of benzalisonitrosoacetoxime,—



melting at 201—202° C. These were sparingly soluble in alcohol, chloroform, and acetone, soluble in glacial acetic acid, and insoluble in absolute ether. When the oxime was suspended in absolute ether, and treated at a low temperature with nitrogen peroxide, a light flocculent precipitate of nitrate benzalmethylglyoximehyperoxide,—



which melted when pure at 101—102° C. It was insoluble in dilute sodium hydroxide, and did not reduce Fehling's solution in the cold. When this substance was slightly heated in benzene solution, or in glacial acetic acid solution, it was decomposed with the evolution of red fumes and the formation of benzalmethylglyoxalketoxime, $\text{C}_6\text{H}_5\text{CH}=\text{CH}.\text{C}=\text{NOH}.\text{CHO}$. When re-crystallised from absolute alcohol, and subsequently from benzene, benzalmethylglyoxalketoxime separated in the form of slightly brown needle-shaped crystals melting at 103—104° C. It was easily soluble in chloroform, acetone, benzene, and glacial acetic acid, and was soluble in ether. It reduced Fehling's solution in the cold and was soluble in dilute sodium hydroxide and in dilute nitric acid. When acted on by semicarbazide, it yielded two isomeric semicarbazones, one of which was easily soluble in glacial acetic acid and melted at 225—226° C., and the other, which was insoluble in all the usual organic solvents, melted at 242° C.

Hence, by preparing the oxime of benzalisonitrosoacetone, treating this with nitric peroxide, and decomposing the resulting compound by heating it in benzene solution, the interesting transformation of benzalisonitrosoacetone, $\text{C}_6\text{H}_5\text{CH}=\text{CH}.\text{CO}.\text{CH}=\text{NOH}$, into the isomeric benzalmethylglyoxalketoxime, $\text{C}_6\text{H}_5\text{CH}=\text{CH}.\text{C}=\text{NOH}.\text{CHO}$, was accomplished.

When benzalisonitrosoacetone was dissolved in absolute ether and treated in a freezing mixture with nitrogen peroxide, benzalisonitrosoacetone pseudonitrole, $\text{C}_6\text{H}_5\text{CH}=\text{CH}.\text{CO}.\text{CHNO}.\text{NO}_2$, was formed. It was obtained crystalline from benzene in the form of yellow plates melting at 123—124° C., and was very soluble in most organic solvents. It gave Liebermann's nitroso-reaction, and did not reduce Fehling's solution in the cold.

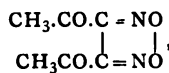
* A Paper read before the British Association (Section B), Southport Meeting, 1903.

Isonitrosoacetone semicarbazone,—

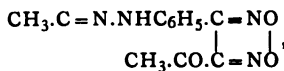


was prepared, and gave white crystals melting at 219—220° C. It gave Liebermann's nitroso-reaction, and was insoluble in concentrated sodium hydroxide and soluble in dilute sodium hydroxide. When heated on a water-bath with acetic anhydride acetylisonitrosoacetone semicarbazone was obtained, which, when re-crystallised from glacial acetic acid, gave cubical crystals melting at 186° C. It dissolved in dilute sodium hydroxide, and when re-precipitated with dilute sulphuric acid, needle-shaped crystals melting at 218—219° C. separated. Hence it was re-converted into the original semicarbazone by the splitting off of the acetyl group. When isonitrosoacetone semicarbazone was treated with nitrogen peroxide at a low temperature, the pseudonitrole of isonitrosoacetone semicarbazone, $\text{CH}_3\text{C}(=\text{N.NH.CO.NH}_2\text{).CH = \text{NO.NO}_2$, was formed. It melted at 163—164° C. with sudden decomposition, and gave Liebermann's nitroso-reaction. It was soluble in dilute sodium hydroxide, giving a yellow solution which was decomposed by dilute sulphuric acid with evolution of nitrogen and oxides of nitrogen.

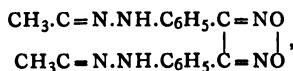
When isonitrosoacetone, $\text{CH}_3\text{CO.CH = NOH}$, in absolute ether solution was acted on by nitrogen peroxide at a low temperature, and the residue left on evaporation of the ether heated with benzene, red fumes were evolved and diacetylglyoxime hyperoxide,—



was produced as a yellow oil. On treating this with phenylhydrazine, the monohydrazone,—



was obtained in the form of yellow rhombic plates melting at 161—162° C. When the monohydrazone was heated with phenylhydrazine, or when the oil was treated with excess of phenylhydrazine, pale yellow rhombic plates of the dihydrazone,—



were formed which melted at 176° C.

FURTHER INVESTIGATION ON THE DETECTION AND APPROXIMATE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC IN MALT, BEER, AND FOOD STUFFS.*

By WILLIAM THOMSON, F.R.S.E., F.I.C.

SINCE my paper on this subject, read before the Manchester Section of the Society of Chemical Industry on May 2nd, 1902, and published in the *British Food Journal*, 1902, vol. iv., Nos. 44 and 45, and in the *Medical Chronicle* for October, 1902 (also in *CHEM. NEWS*, vol. lxxxvi., p. 179), I have continued the investigation with the view of improving on the process there described for detecting and estimating minute quantities of arsenic.

Wrapping the Heated Portion of the Tube in Copper Wire Gauze.

It was recommended by the Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts, that a piece of copper wire gauze about one inch square be wrapped round the tube which receives the mirror at the point at which it is heated (immediately before the drawn-out portion). I directed my attention to find what advantage this offered over the heating of the naked glass tube, and ascertained that the use of the copper wire gauze was a positive disadvantage, the mirrors being less distinct with, than without, the wire gauze. Fig. 2 (a) shows photographic production of the mirrors in three tubes, which were obtained from 50 c.c. of a solution containing $\frac{1}{100}$ of a grain per gallon of arsenic trioxide, As_2O_3 , in which the naked tube was heated, whilst Fig. 2 (b) shows photographic productions of mirrors in three tubes in the production of each of which 50 c.c. of the same solution were used, but where the heated portion of the tube was wrapped in one layer of copper wire gauze, as recommended by the Joint Committee. It will be seen on comparing these two series of tubes, that in each case more distinct and reliable mirrors are obtained by heating the naked tube than by heating it when wrapped in wire gauze.

I tried to determine the temperature at which small quantities of arsenic would be deposited from arseniuretted hydrogen, mixed with free hydrogen by placing the tube for receiving the mirror at right angles through an iron tube, underneath which was a Bunsen flame which was

* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlvii., Part 6.

FIG. 1.

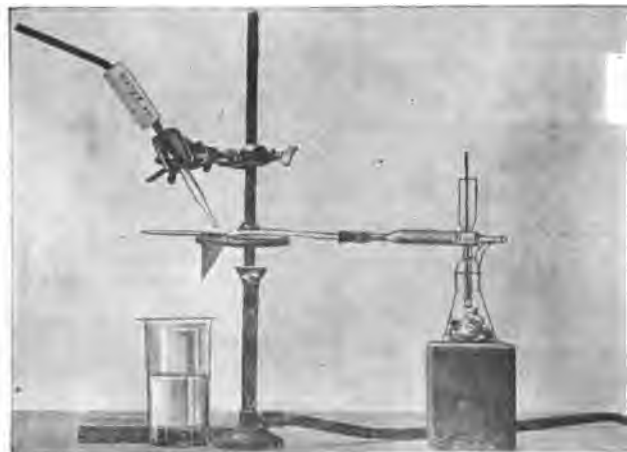


FIG. 2.

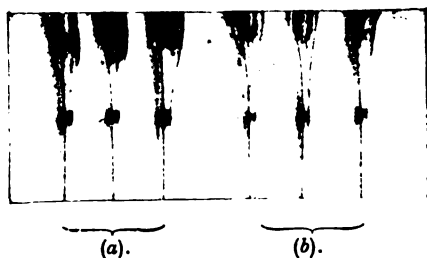


FIG. 3.

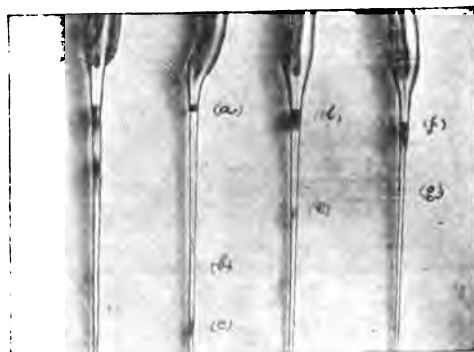
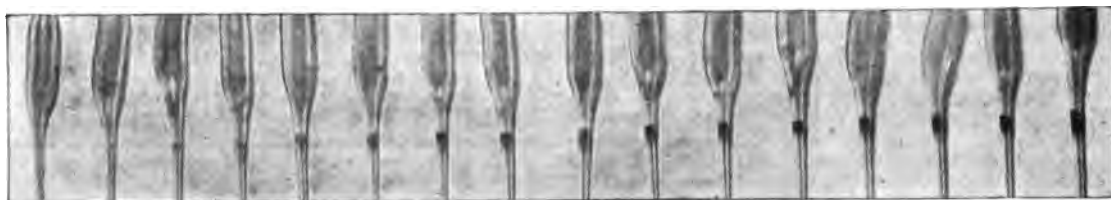


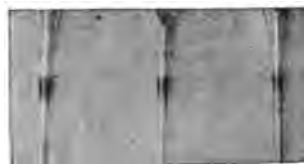
FIG. 4.



Free Acid 1/2000 1/1000 1/666 1/500 1/333 1/250 1/200 1/166 1/143 1/125 1/111 1/100 1/88 1/66
& Zinc. (Grains per gallon).

FIGS. 5 and 6.

Hydrogen.



Open.
1 2

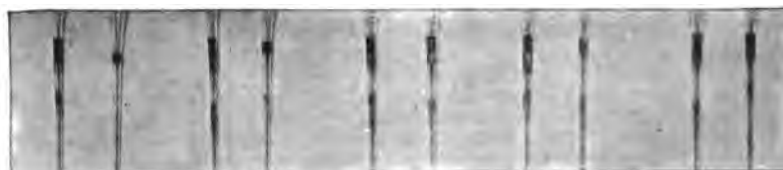
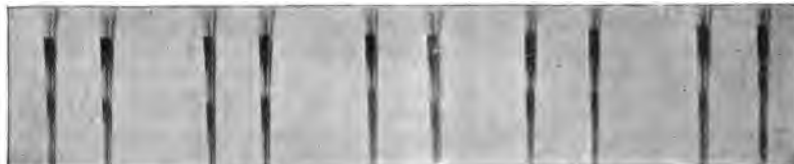
Air.
3 4

FIGS. 7 and 8.

Hydrogen.
5 6

Nitrogen.
7 8

Carbon dioxide.
9 10



gradually raised, but I found that when heated to the full safety range of my thermometer, viz., 393° C., no trace of arsenic mirror was produced on the cooled part of the drawn-out portion of the tube. This result does not confirm the statement made in D. Mendeléeff's "The Principles of Chemistry" (English edition, 1897), vol. ii., p. 182, where he says, in speaking of arseniuretted hydrogen:—"But its presence in the most minute quantities may be easily recognised from the fact that it is easily decomposed by heat (200° C. according to Brunn) into metallic arsenic and hydrogen."

The gas containing arseniuretted hydrogen requires to be

heated to a very high temperature before all the arsenic is deposited as a mirror, and it appears evident that the wire gauze prevents the attainment of the necessary temperature for the complete decomposition of all the arseniuretted hydrogen present.

Influence of Temperature at the Drawn-out Portion of the Tube on which the Mirror is Deposited.

With the view of obtaining information as to this, I used for each of the following tests 50 c.c. of a solution containing $\frac{1}{4}$ of a grain of arsenic trioxide per gallon.

The tubes used are rather wider at the drawn-out parts

than those which I now prefer to use, the first mirrors forming at a point having an internal diameter of about 0.063 of an inch (1.6 m.m.).

Tube No. 1, Fig. 3, shows the photographic representation of the mirror obtained in the ordinary way, by heating the naked tube with the top of a Bunsen flame 4 inches long, protected from draughts by a conical chimney to within an inch of the top of a flame, as previously described by me. It will be observed that two deposits have formed near to each other. The first has a brownish metallic appearance, and the second is black.

The result of the second experiment is shown in tube No. 2 in this series. This tube was enclosed in another tube between the points (a) and (b), kept at 100° C. by passing a current of steam through it, and half-an-inch from the end of the steam jacket the tube was cooled by means of a piece of tissue paper over which a current of cold water was kept rapidly dropping.

It is remarkable that the temperature of boiling water prevented the formation of the mirror altogether. The small ring of mirror formed just outside the beginning of the steam jacket, whilst the uncondensed arsenic passed for half-an-inch along the tube outside the steam jacket without depositing, and only made its appearance as a black deposit at the point (c) where it came in contact with the cooling effect of the stream of cold water.

The outside of the tube No. 3 in the series was covered with one layer of tissue paper from (d) to (e), and a stream of water at 50° C. was kept flowing over it. It is remarkable that at this temperature the bulk of the arsenic was deposited at the point where the comparatively hot water flowed over the tube, and it is curious to observe that on the further portion of the tube heated to this temperature no further mirror formed, but when the gas passed along the tube to the part which was not heated (to 50° C.) a second faint black deposit was formed, and, after leaving an interval of the tube free from deposit, a third, still fainter, black deposit made its appearance.

The tube No. 4 in this series was cooled by placing over it between the points (f) and (g) a single layer of tissue paper, which was cut into a triangular shape at the bottom, and over which water at 15° C. was kept rapidly dropping, as shown in Fig. 1. In this tube only one mirror was formed at the point where it came in contact with the cooled tube.

It was evident, then, first, that the cooling of the tube was an important condition for obtaining the largest mirrors; secondly, that when the tube was cooled to about 15° C. only one mirror formed; thirdly, that that mirror had a metallic lustre, and no second or third black deposit ever formed on any other part of the tube.

Since making these experiments I find that two other chemists have drawn attention to the importance of cooling the portion of the tube arranged for receiving the mirror, the first being Gabriel Bertrand, who employs a strip of filter-paper 4 to 5 m.m. wide wrapped two or three times round the tube, and fed with water drop by drop; and the second A. Gautier (*Bull. Soc. Chim.*, 1902, p. 27; 20, 21), whose method consists in applying a brass rider, the lower part of which is kept immersed in crushed ice.

My experience has shown that the best results have been given by a piece of tissue paper 3 or 4 inches long by $\frac{1}{4}$ -inch wide, folded in the centre, and hung over the tube for receiving the mirror, over which water is allowed to drop rapidly, the two hanging folds being cut to a point to allow the water to run off in a single stream into a glass placed underneath. A roll of several layers of filter-paper is not so effective for cooling, as the cold water takes some time to penetrate the several layers of paper.

Brown-metallic looking Mirrors and Black Arsenic Deposits.

It has been suggested by the Joint Committee above mentioned, and by other chemists, that the presence of oxygen or air, if mixed with the hydrogen from the generating apparatus, tends to produce black deposits rather than metallic arsenic mirrors; this seems to be so,

but the explanation appears to be that the heat produced by the burning of the oxygen and hydrogen at the red-hot portion of the tube, evaporates the mirror after it has been deposited in the brown-metallic condition, and it then deposits a little further on in the black form. On gently warming the brown-metallic mirror with a small Bunsen flame, whilst the hydrogen is still flowing, the metallic mirror is evaporated and deposited a little further on as a black deposit. I have tried thus converting the metallic mirrors into black deposits, with a view to ascertain whether such deposit would form a better measure of the quantity of arsenic present than the metallic mirror, but have found that the quantities are better indicated by the brown-metallic mirrors than by the black deposit.

I have studied somewhat more minutely these two forms of arsenic. The first, or brown form, with metallic lustre, is that which is crystalline and firmly adherent to the glass tube; the second, or black form, is amorphous, and can easily be removed from the tube by gentle rubbing.

I was led to believe that the amorphous form contained occluded gaseous matter, and I have spent some time in collecting a quantity of it (several grms.), which was placed in a tube from which the air was exhausted by a Töpler pump, which is the method employed by Sir William Ramsay for removing helium from various minerals. After the tube was exhausted till no further gas could be drawn from it, the black arsenic was heated, and it volatilised and condensed in the crystalline form, but no trace of gaseous matter was liberated from it.

Internal Diameter of the Tube upon which the Arsenic Mirror is Deposited.

As the tubes used by me are all drawn out in the same manner from previously selected tube, they are found to be very closely the same in the internal diameter of the bore, but, as these tubes are slightly conical, I devised a simple measuring arrangement for obtaining the mirrors on exactly the same internal diameter of tube. This consists of an iron wire with the one end thinner than the other; the thicker end is first put into the drawn-out portion of the tube and then the thinner end, to see that the difference in the distance between which they enter is about $\frac{1}{4}$ of an inch, which it generally is, although the distance of the wider portion from the beginning of the drawn-out part varies slightly; the tissue paper for cooling is then placed so that the edge nearer the flame is exactly at the point where the entrance of the thicker end of the wire is arrested, and the mirrors, being all deposited at this point in the different tubes (where the cold water comes in contact with the glass), more accurate measures of the quantities of the deposits are obtained.

With the view of keeping the tubes hot to the point at which the cold water comes in contact with the narrow glass tube, to prevent the formation of a mirror before the portion of the tube is reached on which it should be deposited, I put a small coil of copper or platinum gauze $\frac{1}{2}$ of an inch square around the tube, so as to cover the rounded part of the drawn-out portion and part of the narrow tube to within $1\frac{1}{2}$ m.m. of the paper. I use a flat Bunsen flame one inch wide, the flame acting on about $\frac{3}{4}$ of an inch of the uncovered glass tube, with the end of the flame playing on the wire gauze.

Fig. 4 shows mirrors obtained by the cooling process on the tubes of accurately measured internal diameter.

The apparatus employed for carrying out the process is shown in Fig. 1.

Fading of the Arsenic Mirrors and Black Deposits.

In my previous papers on the approximate estimation of arsenic, I have mentioned that I had not observed that any of my arsenic mirrors had faded even when exposed to air and light, but, as other chemists had had experience of fading, and had recommended the sealing of the mirrors in an atmosphere of hydrogen to prevent it, I considered it desirable to carry out this process, and have since done so.

I was much surprised, however, to find that the mirrors which were made by the old process, and the original photographs of which are seen in Fig. 5, faded after exposure to the light for six weeks; a second photograph of the same, taken after exposure, is shown in Fig. 6.

It is difficult to imagine why these arsenic mirrors and deposits should have wholly or partially disappeared after being sealed up in an atmosphere of hydrogen. It is curious, however, that, whilst the mirror from the middle tube has entirely disappeared, those in the first and third tubes have only partially faded.

Other instances of fading are shown in the photographs Figs. 7 and 8, all the deposits being obtained by the old process, in which the tubes were not cooled with water. The tubes Nos. 1 and 2 were unsealed, 3 and 4 were sealed in air, 5 and 6 in hydrogen, 7 and 8 in nitrogen, and 9 and 10 in carbon dioxide, the mirrors being from the same amount of arsenic solution. The tubes 2, 4, 6, 8, and 10 were detached from the card and exposed to the light for one month, the others being kept in the dark; they were then re-mounted, and again photographed. It will be seen in Fig. 8 that the mirrors in tubes 2 and 4 (exposed to the air) and in 8 (exposed to pure nitrogen prepared by heating ammonium nitrite, and passing the same through a tube containing copper gauze heated to redness) have faded considerably, while in tubes 6 and 10 (in hydrogen and in carbon dioxide) the black or second portion of the deposit only has faded. The mirrors formed by the cooling process appeared to have suffered no change in hydrogen.

My modified and new process affords a much more accurate method of approximately estimating minute quantities of arsenic, and it is much more delicate than the process previously employed; it is, in fact, so delicate that I have now failed to get any zinc which is absolutely free from any trace of arsenic. A very distinct mirror is formed with the $\frac{1}{100}$ th of a grain of arsenic trioxide per gallon, when working with 50 c.c.; that is one part in 140,000,000 parts of liquid, and half that amount can be detected; that is, one part in 280,000,000, which is equivalent to 1 grain of arsenic trioxide dissolved in 4000 gallons of beer; i.e., 1 grain dissolved in 111 barrels of beer of 36 gallons each, which is equivalent to 18 tons weight of beer.

EXPLANATION OF FIGURES.

FIG. 1.—Apparatus employed.

FIG. 2.—Photographic production of mirrors. $\frac{1}{100}$ th gr. per gallon of As_2O_3 when using 50 c.c.

(a) With the naked tube, heated directly with Bunsen flame.

(b) With the heated portion of the tube wrapped in wire gauze.

FIG. 3.—Showing the effect of temperature on the formation of the mirrors and arsenic deposits in a solution containing $\frac{1}{100}$ th of a grain per gallon of As_2O_3 , when using 50 c.c.

1. Ordinary Marsh test method (without special cooling).
2. Enclosed in a steam jacket from (a) to (b), and cooled with cold water at (c).
3. With current of water at 50° C. passing over the outside of the tube between (d) and (e).
4. With current of water at 15° C. passing over the outside of the tube between (f) and (g).

FIG. 4.—Standard bore tubes, using 50 c.c. with different quantities of As_2O_3 . Cooling method.

FIG. 5.—Arsenic mirrors before exposure to the light. $\frac{1}{100}$ th gr. per gallon As_2O_3 using 50 c.c.

FIG. 6.—The same mirrors seen in Fig. 5, after exposure to the light for six weeks.

FIG. 7.—Photographs of five pairs of arsenic deposits, made by the old method, respectively unsealed, and sealed in air, hydrogen, nitrogen, and carbon dioxide. $\frac{1}{100}$ th gr. per gallon using 50 c.c.

FIG. 8.—Photographs of same after the right-hand one of each pair had been exposed to the light for six weeks.

THE VOLCANIC DUST OF MONT PELÉE.

By A. B. GRIFFITHS, Ph.D., &c.

MARTINIQUE is an island situated in the Caribbean Sea (14 degrees north latitude and 16 degrees west longitude), and its volcano, Mont Pelée, was extremely active last year. Mr. W. Wilson, Pharmaceutical Chemist, 281, Brixton Road, S.W., kindly sent me a specimen of the volcanic dust which he received from friends in the island. I have submitted the dust to analytical and microscopical examination, and a micro-photograph is enclosed with this note. It distinctly shows the crystalline nature of the dust. An analysis of the dust (dried at 120° C.), yielded the following result:—

Silica	55.01
Aluminium oxide .. .	20.50
Calcium oxide .. .	9.00
Ferric oxide .. .	3.20
Ferrous oxide .. .	4.86
Manganous oxide .. .	0.25
Magnesium oxide .. .	3.06
Potassium oxide .. .	0.65
Sodium oxide .. .	2.01
Titanium oxide .. .	0.68
Sulphuric oxide .. .	0.42
Phosphoric oxide .. .	0.20
Chlorine .. .	0.16
Copper, nickel, lithium traces	

100.00

Mont Pelée dust has a specific gravity of 2.7211, and contains 3.24 per cent of magnetic material.

Mr. W. J. Townsend and others believe that the wet summer has been caused by Mont Pelée. The black steam-clouds travel in the path of the trade winds over the Gulf Stream, and "there are thousands of tons in the air still waiting to trouble us. So look out for a wet autumn and snowy winter."

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 23rd, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER ON "The Bending of Magnetometer Deflection-bars" was read by Dr. CHREE.

A theoretical paper contributed to the Society by the present author in May, 1901, proved amongst other results that the bending of the deflection-bar of an ordinary magnetometer, under the combined weight of the bar and its load, must increase the distance between the deflecting and deflected magnets, during a determination of horizontal force, to an extent which is not negligible. This conclusion has been borne out by direct observations made at the National Physical Laboratory on a number of magnetometer-bars, including specimens from the leading makers. The mean results thus obtained are recorded in the present paper. The great majority of the data were derived from direct observations made with a pair of microscopes. But a method is described whereby the necessary information can be deduced without the aid of microscopes from the magnetometer's own readings. The magnetometer is set up exactly as in an ordinary deflection experiment, with the deflecting magnet on its carriage at any convenient position on the deflection-bar, and equal weights are hung up symmetrically one on each arm. The consequent increase in distance between the two magnets diminishes slightly the deflecting force on the deflected magnet, and a slight change of

reading is observed in the magnetometer-telescope. The weights are put off and on several times, and the mean change of reading determined. As a check, it is well to observe at two distances. From the change of reading it is possible to determine the increase in distance between the two magnets. In many magnetometers the increase in distance due to the bending is roughly proportional to the distance itself. In the case of bars by the Cambridge Instrument Company the bending increased the distance by almost exactly 1 part in 10,000 at all distances. It is hoped that the method employed will prove useful to magnetic observers who have not ready access to a physical laboratory.

Prof. S. P. THOMPSON said that Dr. Chree had pointed out an important matter in magnetometry, and had told us of the existence of various sources of error. He asked why instrument makers could not design a better instrument, referring especially to the deflection-bar itself, which he said was not of a good form from an engineering point of view. Could not the bending be considerably reduced by making the bar in the form of a girder? Would it not be an advantage to lessen the weight of the carriage by making it of aluminium or of some light alloy? Prof. Thompson said that although the error referred to by the author of the paper seemed large, yet it could not be greater than errors arising from inaccuracy in the setting of the carriage or from other causes inherent in a deflection-experiment.

Dr. W. WATSON expressed his interest in the paper, and said he had never before appreciated the magnitude of the error due to the bending of the deflection-bar. In the many determinations of horizontal magnetic force which he had carried out, he had increased the effect by placing the thermometer near to the magnet on the same side of the magnetometer. He did not think it would be an advantage to lighten the carriage too much, because of the wear and tear which an ordinary magnetometer must be capable of withstanding. With regard to the accuracy of the setting of the carriage, he said that it was not easy to set it to 0.1 m.m., but that inaccuracies of setting to a certain extent compensated each other. Dr. Watson also pointed out that the position of the magnet in the carriage was not always absolutely the same.

The CHAIRMAN pointed out that the method described in the paper might be used to determine Young's modulus by bending the bar with magnets of known weight. A large number of errors entered into the determination of horizontal force, and they were being investigated one by one at the National Physical Laboratory.

Dr. CHREE, replying to Prof. Thompson's remarks, said that various attempts had been made to get rid of the bending effect. The difficulties were due to the fact that it was necessary that the bar should lie in one vertical plane, and that it should pass through the centre of the magnetometer. The error might be reduced by bending the bar so as to make the distance of the magnet from the neutral axis small, but the introduction of corners rendered the theoretical treatment of the problem difficult, and a bent bar was difficult to measure practically. In some of the magnetometers used on the United States Coast and Geodetic Survey, the deflection-bar consisted of two parts pinned together at the centre of the instrument, and although this arrangement had advantages, a great deal depended upon the pin fitting tightly. He contended that if the bending effect could be measured accurately, its magnitude was of minor importance. In the magnetometers used on the Indian Survey, the carriages were much heavier than those in use on ordinary unifilar, and the deflection-bar was constructed something like a girder. There were many causes of error in a force experiment. The formulæ used were complicated, and much depended upon an accurate knowledge of the constants P and Q.

A paper "On the Magnetism of Basalt and the Magnetic Behaviour of Basaltic Bars when heated in Air" was read by Dr. G. ALLAN.

Bars cut from basalt obtained from Rowley Regis and

from Linz, Germany, were tested by means of a magnetometric method to determine their magnetic properties at temperatures from 15° to 800° C. Hysteresis curves are given, and the temperature-permeability curves show that whilst the English basalt has, in general, a maximum permeability near 500° C. followed by a minimum about 550° C., the temperature of maximum permeability in the case of the German basalt lay in the neighbourhood of 50° C., there being a subsequent gradual loss of strength with rise of temperature. Sections of heated and unheated rocks are given, showing evidence of chemical change in some of the rock constituents, and a table of values of susceptibility of the specimens is appended.

The CHAIRMAN expressed his interest in the paper, and said that Dr. Allen had given interesting data which would be of value in the subject of terrestrial magnetism.

Prof. W. F. BARRETT, in a letter sent to the Secretaries, said that Dr. Allan's paper was one of great interest and considerable importance, and he wished to congratulate the author on the results of his laborious investigation. Several years ago he (Prof. Barrett) examined the magnetic properties of various specimens of columnar basalt which had been taken from the Giant's Causeway in Co. Antrim, and a note on the results of this investigation was published in the *Proceedings of the Royal Dublin Society* for Dec., 1899. Each block was found permanently magnetised with a strongly marked north and south pole, the magnetic axis running diagonally through the block, and inclined to the horizon approximately at the angle of dip. As the blocks formed part of vertical columns in the Causeway, their magnetisation was undoubtedly due to the earth's magnetic field, the concave end of each block—for the ends are not plane but slightly concave or convex—was (in all the blocks examined) found to be a north-seeking pole, and must therefore have been downwards when *in situ* at the Causeway. The weight of the blocks varied from 24 to 37 kilograms, and the specific gravity of a fragment of one of them was found to be 2.86. With such large, irregular and feebly-magnetised masses only a very approximate estimate of the magnetic moment was possible by the ordinary method. This was, however, attempted, the blocks being placed on a turn-table with their centres 60 c.m. distant from the reflecting magnetometer. As might be expected, the magnet moment per grm. was found to be very small and almost alike in each side. The volume of the blocks being known, their permanent intensity of magnetisation was found to be less than that estimated by Everett for the earth, regarded as a uniformly magnetised body, viz., 0.079. Nothing could be inferred from this, as the blocks had been removed a long time from the Causeway and had been lying about in different magnetic positions to that which they originally occupied. The long retentivity of the direction of their original magnetisation in spite of rough usage was, however, somewhat remarkable.

Dr. WATSON then showed some Experiments with Electrical Oscillations.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, September 2, 1903.

F. B. GUTHRIE, F.I.C., F.C.S., President, in the Chair.

"The Separation of Iron from Nickel and Cobalt by Lead Oxide (Field's Method)." By T. H. LABY.

The accurate separation of iron from nickel and cobalt is peculiarly difficult.

Review of Methods.

Ammonium Hydrate and Chloride.—The ferric hydrate precipitate carries down so much of the nickel and cobalt present as to require three re-precipitations.

Ammonium Carbonate.—This much-recommended separation is long and tedious.

Basic Acetate.—Using a small quantity of acetate to

precipitate the iron, 99 per cent of the nickel or cobalt can be recovered with one precipitation. But it is not readily combined with the electrolytic determination of the nickel, and sometimes the precipitate of iron is very difficult to filter. Several *electrolytic separations* have been devised; but conflicting statements have been made as to their accuracy. Gooch and Medway, using a rotating cathode, have accurately deposited nickel in half-an hour.

Rothe's extraction of ferric chloride by ether is being considerably used. The concentration of the reagents added is of more than usual importance.

Experimental.

An inquiry into the accuracy of Field's method was made, as it had distinct advantages over methods commonly in use, viz., a *single precipitation* of the iron, and the absence, after the removal of added lead, of all reagents, such as sodium or ammonium salts. Combined with the electrolytic determination of nickel or cobalt, the method becomes more rapid than, say, a double precipitation of the iron by the basic acetate process, and the precipitation of the nickel and cobalt as sulphides. Standard solutions of carefully purified iron, nickel, and cobalt nitrates were prepared. With these solutions twenty-two analyses were made, showing a recovery of over 99 per cent of nickel and cobalt, which is a somewhat better recovery than can be made by a single basic acetate separation.

"On the Narraburra Meteorite." By Prof. LIVERSIDGE, M.A., LL.D., F.R.S.

This metallic meteorite, weighing over 70 lbs., was discovered in 1855 on the Yeo Yeo Creek, 12 miles east of Temora, New South Wales, and was exhibited to the Society by Mr. H. C. Russell, C.M.G., Government Astronomer, in 1900. A general account of the characteristics of this meteorite was given, and a series of seven slices which had been prepared so as to show the internal structure of the meteorite from the exterior to the centre. The meteorite was very difficult to cut in places. The crystalline structure is remarkable, and a series of photographs was shown to illustrate the paper.

NOTICES OF BOOKS

The Planning and Fitting-up of Chemical and Physical Laboratories. By T. H. RUSSELL, M.A. London: B. T. Batsford. 1903.

THIS book will be found most useful by those who may be required to superintend the fitting-up of laboratories and science rooms, especially for educational purposes. The author shows an extensive acquaintance with the contrivances in the newest and most complete laboratories of all kinds in this country, and has described the various necessary fittings in great detail, giving many valuable hints as to the best systems to be adopted under various conditions. Careful attention is directed to the best expedients for obviating the many difficulties which arise when the accommodation for science teaching is very limited. The greater part of the book is devoted to the fitting and arranging of chemical laboratories, with many illustrations and plans and elevations, and constant references to the laboratories where the various methods have been adopted. A shorter section deals similarly with physical laboratories, and the last part contains the general principles of the ventilation, warming, and lighting of schools. In an appendix the details of the laboratory arrangements suggested by the Board of Education for secondary day and evening schools are given. Teachers of physics and chemistry, as well as architects engaged in designing laboratories and science rooms, will no doubt find in this book many useful hints and suggestions.

Treatise on Thermodynamics. By Dr. MAX PLANCK. Translated, with the Author's sanction, by ALEXANDER OGG, M.A., B.Sc., Ph.D. London, New York, and Bombay: Longmans, Green, and Co. 1903.

IN this translation of Prof. Planck's book on thermodynamics some necessary alterations of symbols have been made, and the author has also added a few notes, but otherwise the text of the original German edition has been closely followed. The whole subject is surveyed from a uniform point of view, free use being made of the elementary principles of the calculus, and the method of treatment may be described as that in which new laws of physics and chemistry are developed by a process of logical induction, starting from the two fundamental propositions. Thus, after an introductory chapter containing first principles and definitions, the first law is enunciated and explained, and its applications to homogeneous and non-homogeneous systems are considered. A similar process then follows with the second law and its applications to special states of equilibrium. A translation of Prof. Planck's recent paper, "Über die Grundlage der Lösungstheorie," to which allusion is made in the translator's notice, would probably be very useful to English readers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 14, October 5, 1903.

Conditions which Determine the Sign and the Magnitude of Electrification by Contact.—Jean Perrin. —Already noticed.

Heat of Combustion of Organic Compounds considered as Additive Properties.—Alcohols and Phenols, Ether Oxides, Aldehydes and Ketones.—P. Lemoult.—In a former paper the author showed how, by the aid of five fundamental conventions, it is possible to calculate the heat of combustion of sixty carbides,—which heats have also been the object of direct measurement,—and to obtain between the two series of results a satisfactory coincidence. These conventions, the numerical basis of the calculation, are:—

$$\begin{aligned} f(\text{C}—\text{C}) &= 51 \text{ cal.}, \\ f(\text{C}_2=\text{C}_2) &= 130 \text{ cal.}, \\ f(\text{C}_3\equiv\text{C}_3) &= 210 \text{ cal.}, \\ \text{and } f(\text{C}—\text{H}) &= 53 \text{ cal.} \end{aligned}$$

$f(\text{C}_2=\text{C}_2)$ and $f(\text{C}_3\equiv\text{C}_3)$, repeated in the same molecule, losing 40 cal. The author now extends his results to all series of organic compounds.

Action of Phosphorous Acid on Mannite: Mannide.

—P. Carré.—Phosphorous acid reacts on mannite to give an ether which is the result of the union of 2 molecules of acid with one molecule of alcohol. If the action of the phosphorous acid is sufficiently prolonged, the mannite is dehydrated and mannide thus produced, which enters into the reaction in its turn to give a new phosphorous ether. The phosphorous acid is etherified very rapidly by mannide, giving the ether $\text{P}_2(\text{OH})_4\text{O}_2(\text{CH}_2)_2(\text{CHOH})_4$. The etherification, after passing the minimum, rises very slowly and gives, finally, a phosphorous ether of mannide, $\text{P}(\text{OH})_2\text{O}.\text{C}_6\text{H}_9\text{O}_3$. These ethers are monacids to helianthine and phthalein, in the same way as the phosphorous ethers of the other polyatomic alcohols.

Derivatives and Oxidation Products of Nitropyromucic Acid.—R. Marquis.—Nitropyromucic acid can be easily obtained by saponifying ethylic ether by water at 180° , but the employment of sealed tubes can be avoided

by effecting the saponification by means of strong boiling sulphuric acid. A mixture of 1 vol. H_2SO_4 and 1 vol. H_2O boiling at about 150° is the best strength. When the saponification is finished, the whole is diluted with water and the acid extracted from the ether. From the acid are then prepared—Methyl nitropyromucate, nitropyromucyl chloride, nitropyromucic amide, nitropyromucic anilide, and nitropyromucic-*p*-toluide. The oxidation products of nitropyromucic acid are best obtained from the ethylic ether by submitting it to the action of sodium dioxide.

Reduction of Ortho-nitrobenzyl-methylic Ether-oxide.—P. Freundler.—The author's experiments show that *o*-nitrobenzyl-methylic ether is partially saponified by alkalis, thus differing from ordinary ether oxides. This saponification may be attributed to the presence of the electro-negative group, NO_2 —a fact analogous to that already noticed with regard to the phenolic ethers, which are hydrolysed little by little by boiling alcoholic potash.

MISCELLANEOUS.

Institute of Chemistry.—The Council of the Institute of Chemistry have received the Report on the Examination in Biological Chemistry, held from 20th to 23rd of October last. The Examination consisted of practical exercises in bacteriological methods as related to water supply and sewage, the microscopical examination of micro-organisms, the methods of working with and identifying vegetable enzymes, and methods for the identification and quantitative determination of the carbo-hydrates. The Candidates were also examined orally on subjects connected with their work.

Thomas Macara, A.I.C., was recommended for a Certificate in Biological Chemistry, and John Augustus Herman Brincker, B.A., M.B. (Cantab), was recommended for election to the Associateship of the Institute.

The following exercises were given:—

Tuesday, October 20th, 1903.

1. Determine the number of micro-organisms contained in the given sample of contaminated water, and also examine for the presence of *B. coli-communis*.
2. Examine the given sample of garden soil, for the presence of spore-forming anaërobic bacteria.

(NOTE.—These exercises may be continued throughout the Examination, but you must give in your note-book to-day a brief account of what you propose to do in order to complete the exercise).

Wednesday, October 21st, 1903.

Examine the given sample of fungus for the presence of the enzymes, lipase, invertase, and laccase. (Specimens of *Polyporus squamosus* and *Agaricus arvensis* were given).

(NOTE.—This exercise may be continued throughout the Examination, but you must give in your note-book to-day an account of what you propose to do).

Thursday, October 22nd, 1903.

1. The dried yeast given contains the enzyme maltase. Demonstrate its action on maltose (in the presence of toluol as an antiseptic) quantitatively by means of the polariscope. Confirm the formation of dextrose by a cupric oxide reduction determination, and by the preparation of its osazone and the determination of the melting-point of this body.

(NOTE.—This exercise may be completed to-morrow, but you must give in your note-book to-day a brief account of what you propose to do).

2. Continue the first and second day's exercises as required.

Friday, October 23rd, 1903.

1. Examine the pure cultures of the organisms supplied, and report fully on your examination. (Cultures of *Sarcina lutea*, *Schiso-saccharomyces octosporus*, a mucor, and a spore-forming bacterium were supplied). Include in your

examination a measure of the dimensions of the organisms. Submit any stained or other preparations you make to the Examiner for inspection.

2. Complete as far as possible the exercises commenced on the first, second, and third days of this Examination.

MEETINGS FOR THE WEEK.

FRIDAY, 13th.—Physical, 8. (At the Royal College of Science, South Kensington). "Means for Electrifying the Atmosphere on a Large Scale" and "An Arrangement for Driving Mercury Pumps," by Sir Oliver Lodge.

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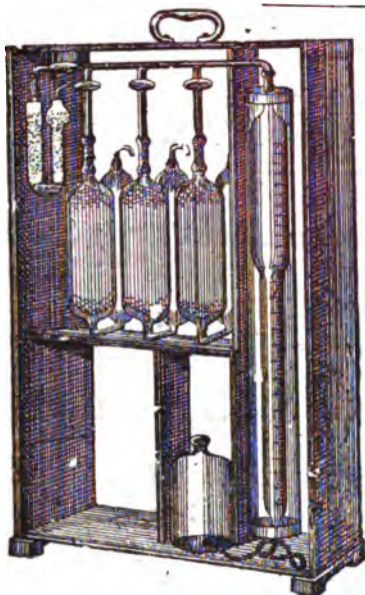
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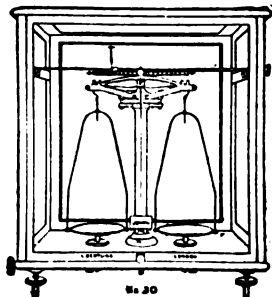
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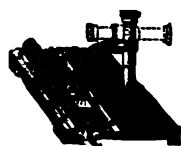
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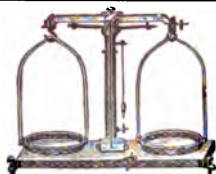
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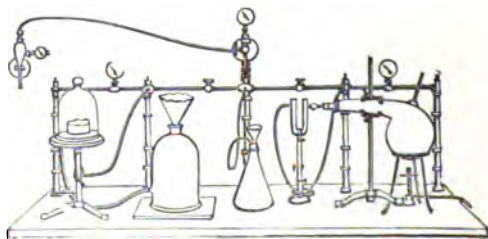
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2294.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 224).

CHAPTER IV.

COMMUNICATION OF RADIO-ACTIVITY TO SUBSTANCES INITIALLY INACTIVE.

DURING the course of our researches on radio-active substances M. Curie and I have observed that every substance which remains for some time in the vicinity of a radium salt becomes itself radio-active. In our first publication on this subject, we confined ourselves to proving that the radio-activity thus acquired by substances initially inactive is not due to the transference of radio-active particles to the surface of these substances. This is proved beyond dispute by all the experiments which will be here described, and by the laws according to which the radio-activity excited in naturally inactive bodies disappears when the latter are removed from the influence of radium.

We have given the name of *induced radio-activity* to the new phenomenon thus discovered.

In the same publication, we indicated the essential characteristics of induced radio-activity. We excited screens of different substances by placing them in the neighbourhood of solid radium salts, and we investigated the radio-activity of these screens by the electrical method. We observed the following facts:—

1. The activity of a screen exposed to the action of radium increases with the time of exposure, approaching to a definite limit according to an asymptotic law.
2. The activity of a screen which has been excited by the action of radium, and which is afterwards withdrawn from its action, disappears in a few days. This induced activity approaches zero as a function of the time, following an asymptotic law.
3. Other things being equal, the radio activity induced by the same radium product upon different screens is independent of the nature of the screen. Glass, paper, metals, all acquire the same degree of activity.
4. The radio-activity induced in one screen by differing radium products has a limiting value which rises with the increased activity of the product.

Shortly afterwards, Mr. Rutherford published a research, which showed that compounds of thorium are capable of producing the phenomenon of induced radio-activity. Mr. Rutherford discovered for this phenomenon the same laws as those just enunciated, besides this additional important fact, that bodies charged with negative electricity become more active than others. Mr. Rutherford also observed that air passed over thorium oxide preserves a notable conductivity for about ten minutes. Air in this condition communicates induced radio-activity to inactive substances, especially to those negatively charged. Mr. Rutherford explains his experiences by the supposition that compounds of thorium, particularly the oxide, give rise to a *radio-active emanation* capable of being carried by air currents and charged with positive electricity. This emanation would be the origin of induced radio-activity. M. Dorn has repeated, with salts of barium containing radium, the experiments of Mr. Rutherford with thorium oxide.

M. Debiegne has shown that actinium causes, to a marked degree, induced activity of bodies placed in its vicinity. As in the case of thorium, there is a considerable carriage of activity by air currents.

Induced radio-activity has various aspects, and irregular

results are obtained when the activity of a substance in the neighbourhood of radium is excited in free air. MM. Curie and Debiegne have observed, however, that the phenomenon is quite regular when operating in a closed vessel; they therefore investigated induced activity in a closed space.

Activity induced in an Enclosed Space.

The active material is placed in a little glass jar, *a*, open at *o* (Fig. 11), in the centre of a closed space. Several plates, *A*, *B*, *C*, *D*, *E*, placed in the inclosure become radio-active after one day's exposure. The activity is the same

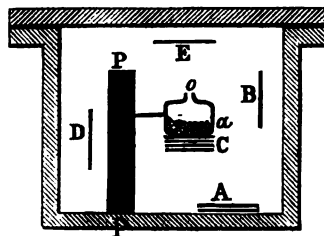


FIG. 11.

whatever be the nature of the plate, for equal dimensions (lead, copper, aluminium, glass, ebonite, wax, cardboard, paraffin). The activity of one face of one of the plates is greater in proportion to the amount of free space about this face.

If the preceding experiment be repeated with the jar, *a*, completely closed, no activity is induced.

The radiation of radium does not directly affect the production of induced radio-activity. For this reason, in the preceding experiment the plate *D*, screened from the radiation by a lead plate of thickness, *PP*, is made as active as *B* and *E*.

Radio-activity is transmitted by the air by degrees from the radiating body to the body to be excited. It can even be transmitted to a distance by very narrow capillary tubes.

Induced radio-activity is both more intense and more regular if the solid radium salt be replaced by an aqueous solution of the same.

Liquids are capable of acquiring induced radio-activity. For example, pure water may be rendered active by placing it with a solution of a radium salt within an enclosure.

Certain substances become luminous when placed in an active enclosure (phosphorescent and fluorescent bodies, glass, paper, cotton, water, salt solutions). Phosphorescent zinc sulphide is particularly brilliant under the circumstances. The radio-activity of these luminous bodies is, however, the same as that of a piece of a metal or other body which is excited under the same conditions without becoming luminous.

Whatever be the substance made active in a closed vessel, this substance acquires an activity which increases with length of time until it attains a *limiting value*, always the same, for the same material and the same experimental arrangement.

The limit of induced radio-activity is independent of the nature and pressure of the gas inside the active enclosure (air, hydrogen, carbonic acid).

The limit of induced radio-activity for the same enclosure depends only on the quantity of radium present in the state of solution, and is apparently proportional to it.

Part played by Gases in the Phenomena of Induced Radio-activity.

Emanation.—The gases present in an enclosure containing a solid salt or a solution of a salt of radium are radio-active. This radio-activity persists when the gas is drawn off with a tube and collected in a test-tube. The sides of the test-tube become themselves radio-active, and the glass

of the test-tube is luminous in the dark. The activity and luminosity of the test-tube finally completely disappear, but very gradually, and a month afterwards radio-activity may still be detected.

Since the beginning of our researches, M. Curie and I have, by heating pitchblende, extracted a strongly radio-active gas, but, as in the preceding experiment, the activity of this gas finally completely vanished.

We could discern no new ray in the spectrum of this gas; this was therefore not a case of a new radio-active gas, and we understood later that it was the phenomenon of induced radio activity.

Thus, for thorium, radium, and actinium induced radio-activity is progressively propagated through the gases, from the radiating body to the walls of the enclosure containing it, and the exciting principle is carried away with the gas itself, when the latter is extracted from the enclosure.

When the radio-activity of radium compounds is measured by the electrical method by means of the apparatus of Fig. 1, the air between the plates is itself radio-active; however, on passing a current of air between the plates, there is no observable lowering of the intensity of the current, which proves that the radio-activity distributed in the space between the plates is of little account in comparison with that of the radium itself in the solid state.

It is quite otherwise with thorium. The irregularities which I observed in determining the radio-activity of the thorium compounds arose from the fact that at this point I was working with a condenser open to the air; the least air current caused a considerable change in the intensity of the current, because the radio-activity dispersed in the space in the vicinity of the thorium is considerable as compared with the radio-activity of the substance.

This effect is still more marked in the case of actinium. A very active compound of actinium appears much less active when a current of air is passed over the substance.

The radio-active energy is therefore contained in the gas in a special form. Mr. Rutherford suggests that radio-active bodies generate an *emanation* or gaseous material which carries the radio-activity. In the opinion of M. Curie and myself, the generation of a gas by radium is a supposition which is not so far justified. We consider the emanation as radio-active energy stored up in the gas in a form hitherto unknown.

Dissipation in Free Air of the Induced Activity of Solid Bodies.

A solid body, which has been excited by radium in an enclosed space for a sufficient length of time, and which has then been removed from the enclosure, parts with its activity in free air according to an exponential law, which is the same for all bodies represented by the following formula:—

$$I = I_0 \left(a e^{-\frac{t}{\theta_1}} - (a-1) e^{-\frac{t}{\theta_2}} \right).$$

I_0 being the initial intensity of the radiation at the moment of withdrawing the plate from the enclosure; I , the intensity after time, t ; a is a numerical coefficient, $a = 4.20$; θ_1 and θ_2 are time constants, $\theta_1 = 2420$ secs., $\theta_2 = 1860$ secs. After two or three hours this law becomes practically a simple exponential, and the effect of the second exponential upon the value of I is negligible. The law of dissipation is therefore such that the intensity of radiation becomes diminished to one-half its value in twenty-eight minutes. This final law may be considered as characteristic for the dissipation in an unconfined air space of the activity induced in solid bodies by radium.

Solid bodies excited by actinium lose their activity in the open air, according to an exponential law similar to the preceding, the dissipation being, however, rather slower.

Solid bodies, made active by thorium, lose their activity much more slowly; the intensity of the radiation is reduced to one-half in eleven hours.

Dissipation of Activity in a Confined Space. Velocity of Destruction of the Emanation.

An enclosure, made active by radium and then removed from its influence, loses its activity by a law which is much less rapid than that of dissipation in the open air. The experiment may be carried out with a glass tube, rendered active internally by placing it for some time in contact with a solution of a salt of radium. The tube is then sealed in the flame, and the intensity of radiation emitted by the walls of the tube is measured while the dissipation takes place.

The law of dissipation is an exponential law. It is given very accurately by the formula—

$$I = I_0 e^{-\frac{t}{\theta}}.$$

I_0 = initial intensity of radiation.

I = intensity of radiation at time, t .

θ = a time constant, $\theta = 4.970 \times 10^4$ secs.

The intensity of the radiation is reduced to one-half in four days.

This law of dissipation is absolutely invariable whatever be the experimental conditions (dimensions of enclosure, nature of the walls, nature of the gas within the enclosure, duration of action, &c.). The law of dissipation remains the same for any temperature between -180° and $+450^\circ$. The law is therefore altogether characteristic.

In these experiments it is the radio-active energy accumulated in the gas that maintains the activity of the walls. If the gas be withdrawn and a vacuum caused in the enclosure, we have found that dissipation of activity at once occurs in the rapid method; the intensity of radiation being reduced to one-half in twenty-eight minutes. The same result is obtained when ordinary air is substituted for the active air in the enclosure.

The law of dissipation with reduction of intensity of radiation to one-half in four days, is therefore characteristic of the disappearance of radio-active energy accumulated in the gas. By making use of the expression adopted by Mr. Rutherford, the emanation from radium may be said to disappear spontaneously as a function of the time, with reduction to one-half in four days.

The emanation from thorium is of another kind, and disappears much more rapidly. The intensity of radiation diminishes to one-half in about one minute ten seconds.

The emanation from actinium disappears still more rapidly; reduction to one-half takes place in a few seconds.

Variation of Activity of Liquids rendered Active and of Radium Solutions.

Any liquid whatever becomes radio-active when placed in an active confined space. On being removed and left freely exposed to the air, the liquid rapidly loses its activity, imparting it to the gas and solid bodies surrounding it. If a liquid thus made active be placed in a closed flask, it loses its activity much more slowly; the latter being reduced in intensity to one-half in four days, just as would a gas under similar circumstances. This fact may be explained by assuming that the radio-active energy is stored in liquids in exactly the same form as in gases (in the form of an emanation).

A solution of a radium salt behaves in a somewhat similar manner. At first, it is a remarkable fact that the solution of a radium salt placed for some time in a confined space is no more active than pure water placed in a vessel in the same enclosure, when the equilibrium of activity is established. If the radium solution be removed from the enclosure and left standing in the air in a wide-necked vessel, the activity spreads itself into space, and the solution becomes nearly inactive, though still containing radium. If this solution be now enclosed in a stoppered flask, it gradually regains, in about a fortnight, a maximum of activity, which may be considerable. On the other hand a liquid made active, but not containing radium, does not regain its activity in a closed flask after having been exposed to the atmosphere.

(To be continued).

THE ATOMIC LATENT HEATS OF FUSION
OF THE METALS,
CONSIDERED FROM THE KINETIC STANDPOINT.

By HOLLAND CROMPTON.*

In considering the changes involved in the passage from the liquid to the solid state as a question of molecular mechanics, the simplest case is that offered by a liquid, the molecules of which are monatomic, or consist each of a single atom only. The possibility of changes occurring inside the molecule may then be regarded as excluded, and we are left with the question of the difference in the relationship of the molecules one to another in the liquid and in the solid state. There seems little reason to doubt that this difference may be regarded as primarily due to the molecules of the liquid possessing a greater freedom of motion than those of the solid. In the passage from liquid to solid it is not at all unlikely, therefore, that there is a considerable loss of molecular kinetic energy, and it is to this point that attention is directed in this paper.

According to the kinetic theory, if a gas is composed of monatomic molecules, on heating the gas the molecules acquire kinetic energy only, and if no outside work is being done this kinetic energy is approximately equivalent to 2.96 calories per degree centigrade for the grm.-molecule. In heating the gas from the absolute zero, at which the molecules would be at rest, to the temperature T , the kinetic energy acquired by the grm.-molecule is then equivalent to 2.96 T calories. Now, in the case of a liquid, although we have at present no means of ascertaining what proportion of the heat given to the liquid is used purely for the purpose of increasing the kinetic energy of the liquid molecules, it would appear probable, more especially from the comparison of the specific heats of gases and liquids, that the amount is the same for liquids as for gases. Therefore, if a liquid is heated from the absolute zero to the temperature T on the absolute scale, the heat utilised in increasing the kinetic energy of the molecules of the liquid would be 2.96 T calories for the grm.-molecule.

Taking then a liquid composed of monatomic molecules, and assuming that the passage from liquid to solid involves a considerable diminution of the kinetic energy of the liquid molecules, the energy thus removed at the temperature T should approximate to 2.96 T calories for the grm.-molecule of the liquid. If no further change takes place the latent heat of solidification of the grm.-molecule should approximate then to this value. Or in other words, if A is the molecular (in this case atomic) weight, r the latent heat of solidification in the usual units, according to the above $Ar = 2.96 T$ or $Ar/T = 2.96$ approximately.

It is possible to submit this result to experimental test as the latent heats of fusion of a number of the metals, presumably of monatomic molecular structure, are known.

In the following table are given the values of r , Ar , T , and Ar/T for those metals for which r has been, up to the present, determined with sufficient accuracy:—

Metal.	r .	Ar .	T .	Ar/T .
Sodium ..	31.8	731	370	1.98
Potassium ..	15.7	613	335	1.84
Copper ..	49.1	3140	1355	2.32
Silver ..	27.0	2920	1230	2.37
Gold ..	16.3	3227	1335	2.41
Zinc ..	28.1	1839	688	2.67
Cadmium ..	13.7	1531	593	2.58
Mercury ..	2.8	505	234	2.41
Aluminium ..	80	2166	927	2.33
Thallium ..	7.2	1470	562	2.61
Tin ..	13.3	1573	503	3.05
Lead ..	6.4	1340	598	2.24
Palladium ..	36.3	3873	1773	2.18
Platinum ..	27.2	5295	2053	2.58
Gallium ..	19.1	1336	286	4.67
Bismuth ..	12.5	2602	540	4.82

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

It will be seen that in the case of fourteen of the above sixteen metals, the values of Ar/T vary from 1.84 for potassium to 3.05 for tin, the average value being 2.4.

There is, therefore, in these cases a moderately close approximation to the predicted value of 2.96. Two metals, bismuth and gallium, give much higher values than the rest, and evidently are not in keeping with the general view here advanced. Whether this is due to these metals not possessing a monatomic structure or to some other cause cannot at present be decided.

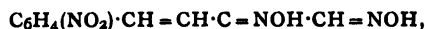
PREPARATION OF OXIMIDO COMPOUNDS.*

By W. SLOAN MILLS, M.A., Queen's College, Galway
(1851 Exhibition Scholar).

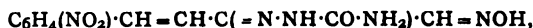
As it seemed desirable that the work described in the paper on "The Action of Oxides of Nitrogen on Oximido Compounds" should be extended to other oximido compounds, *m*-nitrobenzalisonitrosoacetone and cuminalisonitrosoacetone and some of their derivatives were prepared.

Molecular proportions of isonitrosoacetone and *m*-nitrobenzaldehyde were condensed to *m*-nitrobenzalisonitrosoacetone, $C_6H_4(NO_2) \cdot CH = CH \cdot CO \cdot CH : NOH$, by means of sodium hydroxide. A theoretical yield was obtained. When re-crystallised from absolute alcohol it gave slightly yellow coloured crystals, melting at 164° C., which were easily soluble in acetone, ether, and glacial acetic acid. It was soluble in dilute sodium hydroxide. When treated with phenylhydrazine a yellow crystalline hydrazone was formed melting at 99—100° C. When heated on a water-bath with excess of phenylhydrazine a dark red insoluble precipitate was obtained, which melted at 206—207° C., and proved to be the dihydrazone of *m*-nitrobenzal methylglyoxal, $C_6H_4(NO_2) \cdot CH = CH \cdot C : (N \cdot NH \cdot C_6H_5) \cdot CH (N \cdot NH \cdot C_6H_5)$.

m-Nitrobenzalisonitrosoacetoxime, —

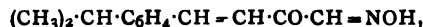


was isolated when the ketone was treated with free hydroxylamine. It is soluble in glacial acetic acid, insoluble in absolute alcohol, and melts at 220° C. By the action of semicarbazide on the ketone *m*-nitrobenzalisonitrosoacetone semicarbazone, —

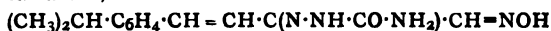


was obtained which melted at 196—197° C.

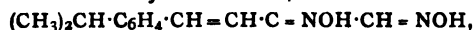
Cuminalisonitrosoacetone, —



was prepared by the condensation of cuminal and isonitrosoacetone. It was re-crystallised from benzene, giving beautiful sulphur yellow rectangular plates melting at 162—163° C. It does not give readily a crystalline hydrazone. It is easily soluble in ether and acetone, soluble in benzene, and insoluble in petroleum ether. By the action of semicarbazide cuminalisonitrosoacetone semicarbazone, —



was obtained, which melted at 176° C. when re-crystallised from dilute alcohol. It is easily soluble in acetone, and soluble in ethyl acetate and ether. When the ketone was treated with free hydroxylamine in methyl-alcohol solution a beautiful white crystalline oxime, —



was precipitated on the addition of a little water. It melted at 192° C., and was easily soluble in ether acetone and ethyl acetate, soluble in alcohol and benzene, and somewhat soluble in chloroform.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

ON THE
"SELF-INDUCTION" SPECTRA OF SILICIUM,
AND ITS ASTRONOMICAL COMPARISONS.*

By Count A. de GRAMONT, Docteur ès Sciences Physiques.

MANY of the silicium lines recognised in stellar spectra have been considered characteristic of a high temperature, and I have thought it would be interesting to study their behaviour under the influence of "self-induction," and to give here that part of the spectrum susceptible of astronomical comparisons. The spectrograms show, on their upper part, the spectrum of the ordinary condensed spark of silicium, obtained with an induction coil giving a 15 c.m. spark and a condenser of 0.009 microfarad; and beneath this spectrum are photographs successively taken with "self-inductions" varying from 0.00002 Henry to 0.03000 H. The spectra were taken with two prisms of heavy flint glass, and subsequently with a calc-spar prism and quartz lenses. The silicium spectrum taken in these circumstances showed two very different categories of rays:—

1. Lines resisting a self-induction of 0.03 H., and even reinforced by it.
2. Lines commencing to grow feeble with a weak self-induction of 0.0002 H., and disappearing almost simultaneously with 0.0062 H.

Lockyer as the most remarkable of the "enhanced lines" of silicium. Under the influence of self-induction they are the last to disappear; spectrograms show that they shorten by concentrating in the vicinity of the electrodes, becoming reduced to points, and vanishing at a self-induction of 0.0062 H.

The line 3905 of the triplet ζ is very strong at the maximum self-induction employed (0.03 H.), while the neighbouring lines, 3862, 3856, scarcely visible at 0.0006 H., disappear entirely before reaching 0.0062 H.

The triplet η (3807 to 3791) appears to disappear at a still feebler self-induction.

The most refrangible part of the spectrum has no astronomical interest, for it is stopped by atmospheric absorption. I have studied it with a quartz spectrograph. The line 2542 disappears with the same amount of self-induction as above; that is to say, at less than 0.0062. All the other lines, especially the characteristic six-line group (2529 to 2507) and the group (2217 to 2208) entirely resist the maximum self-induction. Finally, I have found that the extreme line 1930.0 does not belong to silicium, but to aluminium.

These researches have been made with silicium crystallised in small octahedra and plates, then with sodium silicate fused before the blowpipe on platinum wires. As I have already shown, the effect of self-induction is the same with solid bodies as with fused salts (*Comptes Rendus*, May 5 and 26, 1902).

Permanent with "self"		α	$\left\{ \begin{array}{l} 6370 \\ 6342 \end{array} \right.$	Strong. Strong.	
Disappearing with "self"		β	$\left\{ \begin{array}{l} 5879 \\ 5960 \end{array} \right.$	Easily visible. Easily visible.	
Permanent with "self"		γ	$\left\{ \begin{array}{l} 5059.8 \\ 5045.5 \end{array} \right.$	Strong. Strong.	
Disappearing with "self"		δ	$\left\{ \begin{array}{l} 4574.5 \\ 4567.0 \\ 4552.5 \end{array} \right.$	Well marked. Strong. Strong.	$\left\{ \begin{array}{l} \text{Seen in the very hot helium stars} \\ \text{such as } \beta \text{ Crucis, } \epsilon \text{ Canis Majoris} \\ \text{Bellatrix.} \end{array} \right.$
			$\left\{ \begin{array}{l} 4131.0 \\ 4128.0 \end{array} \right.$	Very strong; diffused. Very strong; diffused.	
Rather reinforced by "self"		ζ	$\left\{ \begin{array}{l} 3905.5 \\ 3862.5 \\ 3856.0 \end{array} \right.$	Very strong and sharp. Rather strong and sharp. Strong; sharp.	$\left\{ \begin{array}{l} \text{Seen in Sirius, } \alpha \text{ Cygni, Rigel, in the} \\ \text{stars of the Groups VI. to VIII. of} \\ \text{the Harvard College classification,} \\ \text{where they accompany the pre} \\ \text{ceding doublet, } \epsilon. \end{array} \right.$
			$\left\{ \begin{array}{l} 3835.0 \\ 3807.0 \\ 3796.0 \\ 3791.5 \\ 3094.5 \\ 3087.2 \end{array} \right.$	Weak. Rather strong. Rather strong. Weak. Rather strong. Rather strong.	$\left\{ \begin{array}{l} \text{Seen in } \epsilon \text{ Canis Majoris with the} \\ \text{groups } \delta \text{ and } \epsilon. \end{array} \right.$

The doublets α and β were measured by sight only with a direct-vision spectrocope. It will be interesting to see if the group β accompanies groups δ and ϵ in the hot stars.

The triplet δ (4574 to 4552) has been recognised by M. Demarçay ("Spectres Électriques," Gauthier-Villars, Paris, 1895) as belonging to silicium in hydrofluoric solution, and by myself with free silicium and in fused silicates ("Spectres des Métalloïdes dans les Sels Fondus: Silicium," *Comptes Rendus*, January 25, 1897). Notwithstanding this, these same lines, recognised by many observers in the spectra of the stars, were not attributed to silicium until 1900, when Mr. Joseph Lunt in his turn showed their origin (*Roy. Soc. Proc.*, lxi., 44).

The doublet ϵ (4131, 4128) is considered by Sir Norman

The wave-lengths have been measured for comparison with the lines of a cadmium-lead alloy, photographed on each of the spectrograms.

Royal Institution.—The Annual Course of Christmas Lectures at the Royal Institution, specially adapted to young people, will be delivered by Professor Ray Lankester, M.A., LL.D., F.R.S., Director of the Natural History Department of the British Museum, whose subject is "Extinct Animals." The first lecture will take place on Tuesday, December 29, at 3 o'clock, and the remaining lectures will be delivered on December 31, 1903, and January 2, 5, 7, and 9, 1904.

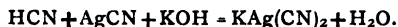
* A Paper read before the British Association (Section B), Southport Meeting, 1903.

THE VOLUMETRIC DETERMINATION OF
MERCURY AND OF HYDROCYANIC ACID.

By LAUNCELOT W. ANDREWS.

It is a familiar fact that hydrocyanic acid is a "pseudo-acid" which possesses no acid reaction at all toward many indicators, as methyl orange, nitrophenol, &c., and which cannot be acidimetrically titrated even with the aid of extremely acid-sensitive indicators, such as phenolphthalein or toluylene red. If silver nitrate is added to a solution of hydrocyanic acid a quantitative precipitation of silver cyanide occurs, and if the silver salt is in excess, an amount of nitric acid is set free equivalent to the hydrocyanic acid used. Titration of the nitric acid by the acid of any suitable indicator, such as paranitrophenol, leads to a knowledge of the amount of hydrocyanic acid originally present. The process is accurate but not especially convenient. The precipitated silver cyanide may retain free hydrocyanic acid or silver nitrate, or both, according to the conditions of the precipitation, semipermeable "cells" being formed which give up their contents very slowly by long-continued washing, and which continue to exhibit an acid reaction even after washing with excessive amounts of water. This difficulty can be brought within bounds by precipitating from highly dilute solutions. It might be thought possible to titrate the free nitric acid directly, without filtering from the precipitate, and such is in fact the best mode of proceeding. Nitrophenol is a good indicator for the purpose, although methyl orange may be used. Lacmoid forms an insoluble compound (silver salt?) which disturbs the sharpness of the end-reaction. If the hydrocyanic acid is in excess, and silver nitrate from a known amount of metallic silver is employed, an exact determinate quantity of nitric acid will be set free, and, hence, the titration can be used for the standardising of acidimetric alkali solutions, the object with which the experiments were originally undertaken. The advantage of using pure metallic silver as the standard is obvious, but the difficulties referred to above, lying in the character of the precipitate, appear here also in an aggravated form. The attempt to titrate the free nitric acid without filtering from the silver cyanide meets with almost insuperable difficulties when the solution contains an excess of hydrocyanic acid.

In this case, as soon as the free nitric acid is neutralised, the complex salt, potassium argentocyanide, KAgCy_2 , begins to form in accordance with the reaction—



Potassium argentocyanide is a neutral salt, so that the reaction of the solution changes from acid to neutral as excess of potassium hydroxide is added, instead of from acid to alkaline, and remains neutral until all hydrocyanic acid is converted into potassium argentocyanide. At the same time, the silver nitrate occluded in the precipitate slowly diffuses out, reacting as it does so with the hydrocyanic acid. It is therefore necessary to filter before titrating, and previous to the filtration a digestion for at least twenty-four hours is necessary, during which time the precipitate must be agitated with the solution. It is not thought worth while to give the details of the long series of experiments, since the final result is that the method, while capable of a high degree of accuracy when all precautions are observed, does not possess the simplicity which can be demanded of such a process.

It appeared to the writer to be a question as to how far the completeness of the reaction between hydrocyanic acid and silver nitrate is due to the insolubility of silver cyanide, and how far to its being, possibly, a compound not subject to electrolytic dissociation; that is, not a true salt at all. If the latter were the dominant factor, it should be possible to secure a practically complete reaction between mercuric nitrate or chloride and hydrocyanic acid, since mercuric cyanide is well known to be a non-dissociated compound. If methyl orange is added in small quantity to a solution of pure mercuric chloride and also to a solution of hydrocyanic

acid, both solutions remain pure yellow, showing no trace of acid reaction. If the solutions are now mixed together, they turn bright red. The experiment makes a striking lecture experiment illustrative of the theory of electrolytic dissociation. Nitrophenol, lacmoid paper, or even a rather insensitive, strongly blue, litmus-paper, can be used instead of methyl orange to show the liberation of hydrochloric acid, i.e., the production of hydrogen ions. The reaction— $\text{HgCl}_2 + 2\text{HCN} = \text{Hg(CN)}_2 + 2\text{HCl}$, is not instantaneous, but is practically complete, and the disturbing factors mentioned above as occurring in the reaction between silver salts and hydrocyanic acid are absent. It appears, therefore, probable that silver cyanide also is a non-dissociated compound, and that the so-called "elective affinity" between cyanogen and silver is a phenomenon due to this fact rather than to the low solubility of silver cyanide, a supposition with which the known fact that an alkali cyanide reacts quantitatively with silver chloride to form silver cyanide is in the best of harmony.

The possibility of the application of these relationships to the acidimetric titration of mercury or of hydrocyanic acid and the cyanides lies very near. In the sequel it is shown that the possibility can easily be realised. It may be said that no new method for the titration of hydrocyanic acid is needed, since that of Liebig (*Liebig's Ann. Chem.*, 1851, lxxvii., 102), as modified by Deniges (*Ann. Chim. Phys.*, 1895 [7], vi., 381), answers all practical requirements. It is to be noted, however, that the application of Liebig's method requires a perfectly clear solution, whereas pharmaceutical preparations of hydrocyanic acid are frequently turbid. The addition of a new and convenient method of titration to the small number of those already known for the determination of mercury cannot be regarded as a work of supererogation, especially when the new method, as is the case with that described, is applicable to the determination of mercuric chloride in the highly dilute solutions of that substance employed by surgeons.

Determination of Hydrocyanic Acid and Cyanides.

For this determination the following solutions are required:—*a*, decinormal solutions of hydrochloric acid and of potassium (or sodium) hydroxide; *b*, a nearly saturated solution of mercuric chloride, containing about 40 grms. of the pure re-crystallised salt per litre. The exact strength of this solution need not be known; *c*, a saturated solution of pure paranitrophenol in water. This is to be preferred to the solution in alcohol often recommended as an indicator. The aqueous solution keeps indefinitely in the light or in the dark.

To determine hydrocyanic acid or a simple cyanide, dilute the solution till it contains not more than about 1 per cent of hydrocyanic acid and add 2 drops of nitrophenol solution. If this imparts a yellow colour, add decinormal hydrochloric acid until the colour has all but disappeared; if it is colourless, add decinormal potassium hydroxide till the solution shows a very pale yellow. Now, add an excess of the mercuric chloride solution (usually 15 or 20 c.c.), stir and allow to stand for one hour at the temperature of the air.

A solution of hydrocyanic acid which had by gravimetric analysis been found to contain 3.40 per cent, was analysed by the above method. For that purpose, 50 c.c. was measured by a pipette into a 500 c.c. flask, filled to the mark, and shaken. Five c.c. of this solution were mixed with 10 c.c. of an approximately decinormal mercuric chloride solution, allowed to stand for an hour, and then titrated as described. Required, 6.30 c.c. of $\text{N}/10$ KOH, equivalent to 0.01704 grm. of hydrocyanic acid, or 3.408 per cent found.

Twenty c.c. of the same solution were mixed with 10 c.c. of an approximately 4 per cent mercuric chloride solution, and the liquid allowed to stand three hours. Required, 25.03 c.c. of decinormal potassium hydroxide, equivalent to 0.0677 grm. of hydrocyanic acid, or 3.385 per cent (on original solution) found.

From the original solution was prepared, by suitable dilution, a semi-normal hydrocyanic acid solution, containing, by calculation, 13.52 grms. per litre. Five c.c. of this solution were mixed with 33 c.c. of the last-mentioned mercuric chloride solution, and, after standing fifteen minutes, were titrated in the usual way. Required, 24.78 c.c. of decinormal potassium hydroxide, equivalent to 0.06703 gm. of hydrocyanic acid, or 1.34 per cent found. The small deficit observed here is probably due to a slight volatilisation of hydrocyanic acid during the manipulations incidental to dilution and exposure.

Determination of Mercury.

The only solution required, in addition to those mentioned above, is an approximately normal solution of hydrocyanic acid neutral to nitrophenol. Such a solution may be conveniently prepared in the following way without distillation:—Dissolve 68 to 80 grms. of the best commercial potassium cyanide in 0.5 litre of water, add about 5 grms. of barium chloride in saturated solution, and filter, thus removing carbonates which would interfere with the exact neutralisation. To the filtrate add about 10 c.c. of the nitrophenol solution (*vide supra*), and then dilute sulphuric acid till the yellow colour has become pale, finishing the neutralisation with decinormal hydrochloric acid. Finally, make up to a litre, disregarding the barium sulphate, which may be allowed to subside. This solution should contain about 27 grms. of hydrocyanic acid, and be colourless.

The mercury to be determined must be present as mercuric chloride (or bromide?). If in the form of nitrate, a small excess of sodium chloride is added. Organic acids must be absent. It is next to be made neutral by addition of nitrophenol, avoiding undue excess, and hydrochloric acid, till the yellow colour is just on the point of disappearing. To the solution so prepared an excess of the neutral hydrocyanic acid solution is added, and the mixture set aside for not less than one hour for the completion of the reaction. The hydrochloric acid formed is titrated with potassium hydroxide, decinormal or centinormal, according to the dilution of the mercuric solution, until a permanent pale yellow tint is visible. A very small excess of hydrocyanic acid suffices, and an unnecessary excess is for obvious reasons to be avoided. To be sure that sufficient hydrocyanic acid is present, if in doubt add a few drops at the conclusion of the titration. This will instantly destroy the yellow colour if insufficient had been present, but otherwise will not affect it. The method has been repeatedly used by students in this laboratory with very satisfactory results, in part for the determination of mercuric chloride in solutions containing one part in ten thousand. They have with it obtained much better results than by the method of Vitali (*Bolletino Chimico Farmaceutico*, 1894, 365) for the examination of dilute solutions, and in considerably less time. Vitali's method consists in boiling the mercuric chloride solution with an excess of sulphurous acid, expelling the excess, and titrating acidimetrically the sulphuric and hydrochloric acids formed. The method is satisfactory for stronger solutions of mercuric chloride, but certain sources of error which are inappreciable in concentrated solution become serious when the solution is highly dilute. These are oxidation of the sulphurous acid by the atmosphere, imperfect expulsion of the last traces of sulphurous acid, reduction of the mercury too far; *i.e.*, to metal. Prolonged boiling is needed to drive off the last of the sulphur dioxide, which passes off rapidly at first, but with extreme slowness when only a little is left. Reduction of the mercurous chloride to metal is hindered by the considerable amount of hydrochloric acid present in more concentrated solutions, but in those of high dilution the amount of acid is insufficient to have this effect. The precipitate in the latter case often becomes grey. All these sources of error lead to the results of the determination being too high.

That the cyanide method also gives correct results with more concentrated solutions is shown by the following test analyses:—

A solution was prepared containing 6.780 grms. of pure mercuric chloride in 500 c.c. It was perfectly neutral to nitrophenol. To 5 c.c. of it, 2 c.c. of a hydrocyanic acid solution (3.4 per cent) was added, and 1 drop of nitrophenol solution. Required, 5 c.c. of decinormal potassium hydroxide, equivalent to 0.0678 gm. found. Twenty-five c.c. of the same solution, with 5 c.c. of hydrocyanic acid, required 25 c.c. of the standard alkali, equivalent to 0.339 gm. of mercuric chloride found. Again, 25 c.c. of the same solution, with 10 c.c. of hydrocyanic acid and 100 c.c. of water, required 25.03 c.c. of the hydroxide, equivalent to 0.3394 gm. of mercuric chloride found.

Since mercuric chloride is a substance which can be easily obtained in a high state of purity and is in every way well defined, it is suited as a standard for acidimetric solutions, the sharpness of the method of titration which has been described making it readily available for this purpose.

The results quoted of themselves show the practicability of this method, of which I shall have something more to say in connection with a discussion of other methods of standardisation.—*American Chemical Journal*, xxix., No. 3.

ON CERTAIN DERIVATIVES OF PICRIC ACID.*

By C. LORING JACKSON and R. B. EARLE.

THE following paper contains a description of some new compounds, not of much importance, which were prepared in our work upon the coloured addition-compounds formed from sodic alcoholates and nitro derivatives of benzol.

Picryl Bromide (1-Brom-2,4,6-trinitrobenzol), $C_6H_2Br(NO_2)_3$.—This substance was prepared in the hope that it would lead to trinitroanisol with less trouble than the common way of making it from picryl chloride. The yield, however, was so small that the method did not prove of value. The process for making trinitroanisol from anisic acid, on the other hand, gave excellent results, and is described in our paper on the coloured addition-compounds.

Twenty-five grms. of 1-brom-2,4-dinitrobenzol were added to a mixture of 500 c.c. of fuming nitric acid, of sp. gr. 1.51, and 200 c.c. of fuming sulphuric acid, of sp. gr. 1.86, and the whole boiled vigorously for about three hours in a flask closed with a glass bulb. At the end of this time most of the nitric acid had been driven off, and the liquid ceased to boil quietly, but began to effervesce slightly, and to give off very dark red fumes. It was then allowed to cool, poured into a large volume of ice-water, and the precipitate formed dried on a porous plate to get rid of adhering oily impurities. The solid was re-crystallised from a mixture of alcohol and benzol until it showed the constant melting-point 122° to 123° , when it was dried at 100° , and analysed with the following result:—

0.2820 gm. substance gave, by the method of Carius 0.1824 gm. argentic bromide.

	Br.
Calculated for $C_6H_2Br(NO_2)_3$	27.37
Found	27.52

The yield was small, not more than 25 per cent of the theoretical, which we ascribe to oxidation during the long boiling, but, if an attempt was made to check this by diminishing the length of the boiling, little or none of the substance was formed. That it is really the picryl bromide was proved by its conversion into trinitroanisol, melting-point 64° , by treatment with sodic methylate.

Properties of Picryl Bromide.—It crystallises from alcohol in large, yellowish-white crystals, consisting of long plates terminated at each end by two planes at an acute angle, which is often truncated. Rhombic plates were also observed. Frequently arborescent, frost-like groups occur,

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science, by R. B. Earle.

with many branches set obliquely to the trunk, and each branch bordered with rhombic plates, giving it a jagged outline. It melts at 122° to 123° , and is freely soluble in benzol or acetone; soluble in alcohol, cold or hot, chloroform, ether, methyl alcohol, glacial acetic acid, or carbonic disulphide; slightly soluble in cold, soluble in hot ligroin; insoluble in water. The strong acids do not act upon it even when hot, nor do cold alkalis affect it, but it is easily attacked by hot solutions of an alkali. Sodid methylete converts it into trinitroanisol, as has been already stated. The best solvent for it is a mixture of alcohol and benzol.

Phenyl Picrate, $C_6H_2(NO_2)_3OC_6H_5$.—A solution of sodid phenylate was prepared by dissolving 0.4 gm. of sodid hydrate in 1.2 grms. of phenol mixed with a little water; 2.6 grms. of picryl chloride were then added to this solution in small quantities at a time, stirring the liquid constantly during the addition. The mass soon took on a dark colour, and much heat was developed. On washing the product with water, a dirty, insoluble mass was obtained, which was crystallised from a mixture of alcohol and benzol until it showed the constant melting-point, 153° , when it was dried at 100° , and analysed with the following result:—

0.1676 gm. substance gave 20.2 c.c. N at 20° and 769.3 m.m.

	N.
Calculated for $C_6H_2(NO_2)_3OC_6H_5$	13.77
Found	13.96

Properties of Phenyl Picrate.—It crystallises from a mixture of alcohol and benzol in yellowish, short, thick prisms, probably of the monoclinic system, which are terminated by two planes at an obtuse angle. It melts at 153° , and is freely soluble in benzol or acetone; soluble in methyl or ethyl alcohol, chloroform, or cold glacial acetic acid, freely soluble in the last when hot; slightly soluble in ether; insoluble in water or ligroin. The best solvent for it is a mixture of alcohol and benzol. Willgerodt prepared this substance, but gives no description of it (*Ber.*, 1879, xii., 1278).

Action of Acetoacetic Ester on Phenyl Picrate.—In an earlier paper (*Am. Chem. Journ.*, xvii., 597) from this laboratory it was shown that the phenoxy groups in dichlorodiphenoxyquinone were easily replaced by malonic ester residues; in fact, this gave the best method of preparing the dichloroquinonemalonate ester. The following experiment was tried to see whether the phenoxy group in the phenyl picrate would also be susceptible of replacement:—A solution of sodid acetoacetic ester was prepared by adding 0.22 gm. of acetoacetic ester to the solution of sodid ethylate from 0.04 gm. of sodium and absolute alcohol, and to this was added a benzol solution of 0.5 gm. of phenyl picrate. The mixture took on a deep-red colour almost immediately, but we do not feel certain whether this was due to the salt of the picrylacetoacetic ester or to the formation of an addition-product (salt of a quinonitro acid). The mixture was allowed to stand twenty-four hours at ordinary temperature, after which it was washed with water in a separating-funnel, and the aqueous washings acidified with dilute hydrochloric acid. The oily precipitate thus obtained was re-dissolved in sodid hydrate, filtered and acidified once more. As the precipitate was still gummy, it was extracted with carbonic disulphide, the extract evaporated to dryness, washed with a little cold alcohol, and re-crystallised from alcohol until it showed a constant melting-point. As this lay at 97° to 98° there can be no doubt that the substance is the trinitrophenylacetoacetic ester discovered by Dittrich (*Ber.*, 1890, xxiii., 2720), and that the phenoxy group is easily replaced by the acetoacetic ester residue.

4-Brom-2-nitrophenyl Picrate, $C_6H_2(NO_2)_3OC_6H_3BrNO_2$.—Two grms. of the sodium salt of 4-brom-2-nitrophenol were dissolved in 50 c.c. of hot alcohol, and 2 grms. of picryl chloride were added to the solution in small portions at a time, with constant stirring. The heavy, yellow, crystalline precipitate formed was filtered out, washed with

water, and re-crystallised from acetone, until it showed the constant melting-point, 232° , when it was dried at 100° , and analysed with the following result:—

0.2009 gm. substance gave, by the method of Carius, 0.0885 gm. argentic bromide.

	Br.
Calculated for $C_6H_2(NO_2)_3OC_6H_3NO_2Br$..	18.63
Found	18.75

Properties of 4-Brom-2-nitrophenyl Picrate.—It crystallises from acetone in short, thick prisms, probably belonging to the monoclinic system, terminated at each end by two planes at an obtuse angle to each other. Its colour is yellowish-white, and it melts at 232° . It turns brown on exposure to the air. It is freely soluble in hot acetone, soluble in it when cold; soluble in hot benzol, slightly soluble in cold; slightly soluble in ethyl or methyl alcohol, chloroform, ether, or glacial acetic acid; insoluble in water or ligroin. The best solvent for it is acetone. It seems to form a coloured addition compound with sodid acetoacetic ester, but this may be instead the red salt of picrylacetoacetic ester, as pointed out in the last section.—*American Chemical Journal*, xxix., No. 3.

THE VOLUMETRIC DETERMINATION OF MANGANESE IN IRON AND STEEL.

By HARRY E. WALTERS.

In the *American Chemical Society Journal*, 1902, xxiv., 1206) there appeared an article by Stehman entitled "The Determination of Manganese in Iron and Steel," in which the author stated that in attempting to replace lead peroxide with ammonium persulphate and titrating with sodium arsenite, the silver salt of course caused trouble. If, however, the silver salt is thrown out of solution before the titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

With the exception of the titration the method is the same as that read by me before this Section in September, 1901. While preparing that method the writer also tried to make a titration method, but without success, as the hot solutions were titrated and the reaction between the excess of persulphate and the silver nitrate caused the results to be high and irregular.

Since the article by Stehman appeared I have doubted the necessity of precipitating the silver as chloride if the solution be cooled before the titration is begun.

In order to prove the correctness of this view a number of samples were taken and treated as follows:—

0.2 gm. of the samples and a standard steel of known manganese contents were weighed off into suitable test-tubes or beakers, and 10 c.c. of nitric acid of 1.20 sp. gr. were added to each. The solutions were heated until the samples were dissolved and all nitrous fumes were driven off. Fifteen c.c. of a solution of silver nitrate equal to 0.02 gm. $AgNO_3$ (1.33 grms. of the salt to 1 litre of water) were added to each. About one-half gm. ammonium persulphate salt was added, and the solutions were heated until the oxidation commenced, and then for about half a minute longer. The solutions were then cooled.

In preparing the iron samples 1 gm. was dissolved in 30 c.c. of nitric acid of 1.20 sp. gr., filtered into 100 c.c. calibrated flask, and diluted to the mark. After thorough mixing 20 c.c. of the solution were transferred to test-tubes or beakers, and a little ammonium persulphate salt added to destroy the combined carbon. Five c.c. of a solution of silver nitrate (4 grms. of the salt to 1 litre of water) and a little more persulphate were added, and the procedure continued the same as for steels.

When the permanganic acid solutions were cold they were treated as follows:—

First Series.—The manganese was estimated colorimetrically.

Second Series.—The silver was precipitated as chloride and the solutions were then titrated with a sodium arsenite solution until the pink colour was destroyed.

Third Series.—The solutions were titrated with sodium arsenite without precipitating the silver as chloride.

Fourth Series.—The solutions were titrated with hydrogen peroxide without precipitating the silver as chloride.

The following results were obtained :—

Steel No.	18	..	0.28	0.27	0.28	0.27
"	17	..	0.47	0.46	0.48	0.47
"	11	..	0.53	0.55	0.54	0.53
"	22	..	0.57	0.59	0.59	0.59
"	26	..	0.40	0.44	0.43	0.43
"	33	..	0.49	0.49	0.49	0.49
"	90	..	0.90	0.92	0.90	0.89
"	47	..	0.43	—	0.43	0.43
Iron, S	..	..	0.19	—	0.21	0.19
"	712	..	0.22	—	0.22	0.21
"	713	..	0.23	—	0.23	0.24
"	716	..	0.24	—	0.24	0.24
"	828	..	0.16	—	0.16	0.15
"	813	..	0.13	—	0.11	0.11
"	829	..	0.18	—	0.17	0.19
Steel No.	68	..	0.73	0.72	0.74	0.74

It will be observed that the results all agree closely whether the silver was separated or not, and that hydrogen peroxide (as was to be expected) may be used as well as the sodium arsenite.

The end-point in all these titrations is not as sharp as might be desired, but I think it is sharper if the silver is not precipitated.

If the silver is not precipitated the titration must be done quickly, as the persulphate and silver nitrate in solution react to reproduce the colour if allowed to stand.—*Proceedings of Engineers' Society of Western Pennsylvania*, xix., No. 7.

THE PREVENTION OF BUMPING.

By HEYWARD SCUDDER.

A SINGLE glass capillary tube when used according to the following directions will stop most cases of bumping that occur in ordinary laboratory work. The method is simple, effective, and introduces into the liquid no foreign substance except glass and one small bubble of air. In order to carry it out successfully the following details of procedure must be carefully observed.

The origin of the use of a capillary is obscure. The earliest published reference that I have found is by Gernez (*Comptes Rendus*, lxxxvi., 472). Since these references are only incidental and therefore difficult to find, it is quite possible that there may be an earlier one. I have tried all the methods published (most of which are only for special cases), and have found none so simple or of such wide application as the one presented here.

The capillary is made by drawing out a piece of glass tubing until the internal diameter is about 0.5 to 1 m.m. A seal is then made by holding the tube horizontally in the edge of the flame of a Bunsen burner, until the walls have melted together. The tube is bent, if necessary, or held horizontally till cold. For most purposes the seal should be about 1 c.m. from the open end of the tube. The tube is cut off at the desired length and the other end sealed to prevent the entrance of liquid. When cold, the tube is placed open end down in the liquid to be boiled. The open end should rest on the bottom of the vessel containing the liquid, and should remain there during use. When liquids of high specific gravity are being boiled, it is necessary, therefore, to have the capillary so heavy that it will not be thrown off the bottom. This weight can be

obtained by drawing out the tube from which the capillary is made only near the seal, or by using a very thick walled tube.

In a general way the theory of the action of such a tube is, that when heated the air in the capillary expands and passes through the liquid in bubbles. The vapour of the liquid gradually replaces the air, and the stream of bubbles is continuous as long as the temperature around the capillary is at the boiling-point of the liquid. This constant bubbling prevents superheating and consequent explosive boiling. It is apparent that the size of the bubble will depend chiefly on the width of the capillary. This should vary with the nature of the liquid. For liquids of low boiling-point or for frothing liquids a narrow capillary is best, while for heavy liquids a wider capillary (even as wide as 5 m.m. internal diameter) is more suitable.

When boiling with a return condenser, the seal of the capillary must be below the surface of the liquid. If the seal is above the surface, cold drops falling back from the condenser will strike the capillary and cause condensation of the vapour inside it, thus stopping the stream of bubbles. To prevent displacement, the capillary should be of such a length that the upper end reaches nearly to the top of the neck of the flask. When the liquid is in a thin broad layer the capillary should be bent at the seal so as to be parallel or nearly parallel to the bottom of the flask. In boiling liquids in a test-tube, care must be taken that the heat is applied at the bottom of the tube. When a solid is being dissolved, or when in the course of a reaction a solid is being precipitated out of solution, the capillary should be examined from time to time to see that the end has not become clogged.

The capillary is useless if completely filled. Therefore it must be cold and empty when placed in the liquid. Care should be taken (especially in the case of liquids that usually bump badly) to protect the flame from draughts, so that the temperature of the liquid shall not temporarily fall below the boiling-point, allowing the capillary to fill.

Other minor changes and precautions may be advisable at times, but it will be found that they depend on the following principles. The capillary must never be allowed to become filled with liquid. The greater the amount of air there is to drive out (depending on the width of the capillary and the distance from the seal to the open end), the longer will it take to get a rapid stream of bubbles of vapour of the liquid. The greater the distance from the seal to the open end, the longer will it take to fill the capillary on cooling.

This method has been in successful use in these laboratories for nearly a year. By its use it is possible to saponify esters by boiling with a 50 per cent solution of potassium hydroxide (using a return condenser) or to boil concentrated sulphuric acid in a test-tube without any bumping. Only two cases have been met with in which bumping persisted after the capillary was introduced. Both were reactions carried out with a return condenser. Although the bumping continued, it was so greatly lessened that the liquid was not thrown out of the upper end of the condenser, and there was no danger of having the flask broken.—*Journal of the American Chemical Society*, xxv., No. 2.

Estimation of Argon in Atmospheric Air.—Henri Moissan.—The author makes use of the property metallic calcium possesses of absorbing all the oxygen and nitrogen in a given volume of air, in order to estimate the argon in various samples of air. He finds that specimens obtained from the interior of continents at altitudes of 0 to 5800 metres contain from 0.932 to 0.935 per cent by volume of argon, a remarkably constant proportion. Specimens from the surface of different seas contain quantities of argon which in general vary more, and are slightly higher than those from inland parts. A single sample taken over the Atlantic Ocean contained 0.9492 per cent of argon.—*Comptes Rendus*, xxxvii., No. 16.

NOTICES OF BOOKS

Physical Chemistry in the Service of the Sciences. By JACOBUS H. VAN'T HOFF. English Version by ALEXANDER SMITH. Chicago: The University of Chicago Press. 1903.

THE debt which the scientific world owes to Prof. van't Hoff, especially in the domain of physical chemistry, is so thoroughly recognised that any lectures given by him will command the interest of a vast number of readers of all nationalities. These nine lectures were delivered in June, 1901, at the invitation of the University of Chicago on the occasion of the decennium of its foundation, and are here reproduced only slightly condensed and with very few alterations from the stenographic report. The subject was divided by the lecturer into four parts. An introductory lecture, before a general educational conference, gave some explanation of the scope and aims of physical chemistry. The subsequent lectures dealt in pairs with its relations to other branches of science and its application to the solution of many problems connected with them. Thus the first two explained the great services it has rendered in the region of pure chemistry, taking as an illustration the study of the changes which carnallite undergoes in presence of water when the temperature is altered, and touching upon the growth of Arrhenius's theory of electrolyte dissociation. The application to the technical problems of industrial chemistry dealt with the study of the phenomenon known as tin disease, and also the behaviour of carboniferous iron, which is graphically represented in a diagram. Under the heading of Physiology the lecturer explained, first, the importance of the theory of solutions, including a short mention of Loeb's work on artificial fertilisation, and, secondly, the chemical changes brought about by enzymes, the fuller investigation of which subject seems to be destined to lead to such exceedingly interesting and valuable results. Finally, the application of physical chemistry to geology introduced the study of the conditions of formation of geological salt deposits.

The French edition ("La Chimie Physique et ses Applications." Paris: Librairie Scientifique A. Hermann) has been prepared from the German by Prof. A. Corvisy. The excellent portrait of the author, which appears as a frontispiece in the English edition, and the plate showing the appearance of a sheet of tin attacked by the tin disease do not appear in the French translation.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. Band IV. 7 and 8 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1903.

THE articles in this number of these *Beiträge* have been contributed by well-known authors, and are full of interest for those engaged in the study of physiological chemistry. Dr. Carl Oppenheimer sends two communications, one written in collaboration with Dr. Hans Aron, on the behaviour of genuine serum towards tryptic digestion, and another on the fate of albuminous substances in the animal body. The results of exhaustive investigations on the precipitation of colloids are described by K. Spiro. In this research the effects of the addition of salt solutions, alcohols, and alcoholic solutions of salts were minutely examined, and are here detailed. A second and third communication on the application of chemical methods of investigation to the lymphatic organs occupies a large part of the number, which also contains a short paper relating to the derivatives obtained from taurine by the action of benzoic anhydride, phthalic anhydride, and other substances. The author, Dr. Siegfried Tauber, found that sodium cholate under suitable conditions acts on taurine, giving rise to a substance the analysis of which did not show great differences from that of taurocholic acid, and was hence led to the conclusion that he had produced a body which was either identical or isomeric with that acid.

Le Point Critique des Corps Purs. ("The Critical Point of Pure Bodies"). By E. MATHIAS. Paris: C. Naud. 1903.

THIS book contains a very comprehensive treatment of the subject, and owing to its temperateness and impartiality deserves to be regarded as an excellent example of what a monograph should be. It opens with an account of Andrews' pioneering work and his classical theory, and thence passes to the description and criticism of the various experimental methods of determining the critical pressure, volume, and temperature, the importance of the optical method of fixing the temperature and density being marked by the specially full treatment accorded to it. Methods of calculation of the critical constants have been carefully examined, and a table is added containing the constants for some 165 substances, mostly belonging to organic chemistry. Since the book aims at sifting evidence and deciding moot points, ample scope is given for the expression of the author's individual opinion, and it must be admitted that he appears to have always stated the case and his views of it with the utmost fairness and justice. The work gives an excellent account of the present state of our knowledge, and the researches which are being carried out to supplement it.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 15, October 12, 1903.

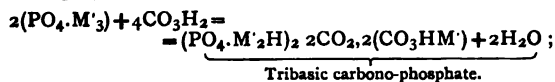
Temperature of Ignition and Slow Combustion of Sulphur in Oxygen and Air.—Henri Moissan.—The ignition temperature of sulphur is 282° in oxygen and 363° in air, both at atmospheric pressure. However, the combustion or slow combination of sulphur with oxygen takes place at a temperature much below that of ignition. Thus, at 100°, this union is manifest after twelve hours. A quantity of sulphur dioxide is produced which, when cooled to -186°, can be obtained in the solid state and identified. This delicate experiment allows of an investigation regarding the phenomenon of combustion with the different varieties of sulphur, even at ordinary temperatures, and it leads to the conclusion that all sulphur, when exposed to air, burns very slowly, giving traces of sulphurous anhydride. The author's series of experiments extend his former researches, and prove that substances such as carbon and sulphur do slowly burn in air at temperatures far removed from their ignition-points.

Electrification of Contact, and Theory of Colloidal Solutions.—Jean Perrin.—It is probable that all colloidal solutions are formed of granules invisible with the microscope, but larger than molecules. The author investigates the causes which assure a stable equilibrium for a certain diameter of molecule, and he proposes a theory that the superficial tension and cohesion tend to the increasing of a granule, but the electrification of such a granule is an internal cause of dislocation, and it may be conceived that there exists a particular diameter for which these two opposing influences are in equilibrium.

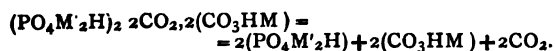
A Series of Bismuth Compounds.—G. Urbain and H. Lacombe.—The authors make a series of experiments which show the analogy between bismuth and the rare earths. They find that bismuth bears the same relation to the rare earths that zinc does to magnesium. A new series of bismuth nitrates are prepared, whose general formula is $3M'(NO_3)_2 \cdot 2Bi(NO_3)_3 \cdot 21H_2O$.

Action of Carbon Dioxide on the Metallic Phosphates under Pressure.—A. Barillé.—The author's ex-

periments prove that when the tribasic phosphates of sodium, ammonium, calcium, barium, and magnesium combine with carbon dioxide under pressure in presence of water, a bibasic phosphate and the corresponding bicarbonate are formed. These results are only obtained after evaporation of the carbonic solution either *in vacuo* or at a moderate temperature. The reaction is shown by the following equation:—

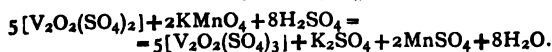


then, further, by dissociation—



The carbonophosphates only exist in solution, and even in this state they always rapidly dissociate when in contact with air.

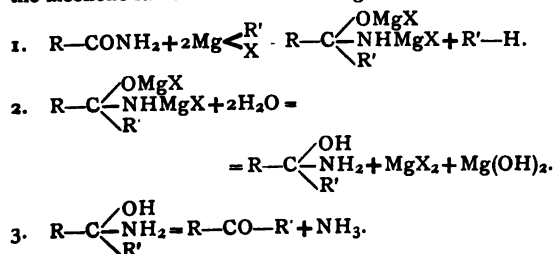
Estimation of Vanadium in Metallurgical Products.—Em. Campagne.—The methods by which vanadium is estimated in the alloys and minerals may be considerably simplified, besides gaining in exactness, by the following modifications:—(1) The ether charged with hydrochloric acid dissolves ferric chloride, whilst it leaves the vanadium oxychloride undissolved; (2) the oxychloride, VOCl_3 , is reduced to VOCl_2 by prolonged boiling with hydrochloric acid, whilst the ferric chloride is not altered. By transformation of the chlorides into sulphates, blue di-vanadyl sulphate, $\text{V}_2\text{O}_2(\text{SO}_4)_2$, is obtained, and ferric sulphate. By titration with permanganate, the quantity of oxygen necessary to transform di-vanadyl sulphate into vanadic sulphate, $\text{V}_2\text{O}_5(\text{SO}_4)_3$, can be found, and from this the amount of vanadium present in the solution estimated. The reactions may be expressed by the following equations:—



Nitric Ethers of Acid Alcohols.—H. Duval.—The author investigates the series of acid alcohols, and prepares the nitrates of the acid alcohols of the fatty series possessing either substituted halogen radicles or not; he then observes their method of decomposition; and, finally, examines the transformation of the nitrotartric ethers into nitrotartronic ethers.

Abnormal Fixation of Trioxymethylene on to certain Aromatic Organo-magnesium Derivatives.—M. Tiffeneau and R. Delange.—The authors investigate the reaction between trioxymethylene and magnesium benzyl chloride, by which a crystalline alcohol is obtained.

Action of Mixed Organo-magnesium Compounds on Amides. New Preparation of Ketones.—Constantine Béis.—When an amide is added to an excess of a mixed organo-magnesium compound, and the whole heated for some hours on a water-bath, ketones are produced. The series of reactions which take place is represented by the following equations, in which R and R' are the alcoholic radicles and X is a halogen:—



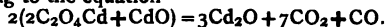
MISCELLANEOUS.

Combined Chemical and Physical Bench.—Messrs. W. and J. George, of 33–37, Hatton Wall, E.C., have recently introduced a combined chemical and physical bench, to meet the growing demand for such in small institutions where space is a consideration and separate rooms cannot be provided for the two subjects. Hitherto the construction of combined chemical and physical benches has only permitted the shelves to be removed for physical work, and it was often difficult to find room for them off the table. Moreover, the risk of carrying a number of shelves containing chemical reagent bottles was considerable. The new form of bench entirely does away with these drawbacks, the shelves being so arranged that, by reversing a catch, they rise up into position when required for chemical work, and by simply pressing them on the top they descend, leaving the table clear for physical experiments. The ordinary drawers and cupboards are of the usual size, and no space is wasted.

Fractional Combustion of Hydrogen, Carbonic Oxide, and Isopentane.—K. V. Charitchkof.—The author has shown previously that Winkler's method of fractional combustion is inapplicable to the analysis of natural gas. In the actual experiment he determines the temperatures of the combustion of pure hydrogen, of isopentane either pure or mixed with hydrogen, and of hydrogen mixed with carbonic oxide. The apparatus has been modified slightly; a thread of palladium-coated asbestos is placed in a tube in the form of a V, which is plunged into an oil-bath, or one of paraffin or tin, according to the temperature it is desired to reach. According to the amount of CO_2 formed, the proportion of isopentane or of carbonic oxide burnt is calculated. The results are given in tables, from which the following conclusions are deduced:—1. Pure hydrogen burns completely at 80° , pure carbonic oxide at about 290° , and isopentane above 395° . 2. The temperature of combustion is the same whether oxygen or air be used; the presence of nitrogen or any other inert gas is without influence on the temperature of combustion. 3. The addition of carbonic oxide or of isopentane raises the temperature of combustion of hydrogen; the influence of carbonic oxide is the greater, although this gas burns at a much lower temperature than isopentane. 4. In a mixture of equal volumes of hydrogen and isopentane, the hydrogen is completely burnt at about 200° , but a proportion of isopentane, varying from 1.6 to 9.2 per cent, is also burnt. 5. The rate of combustion of isopentane is very low; to burn the whole of this gas it is necessary to pass it through the tube containing the palladium-coated asbestos several times. 6. Carbonic oxide behaves almost like isopentane; its presence raises the temperature of combustion of hydrogen as it is present in greater proportion. These results, and, above all, the change of the temperature of combustion of the hydrogen, brought about by the presence of less easily combustible gases, show clearly the inapplicability of Winkler's method.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 461.

Sub-oxides of Cadmium.—S. Tanatar and M. Lévine.—In a previous paper one of the authors has described a sub-oxide, Cd_4O , obtained by heating oxalate of cadmium in a current of CO_2 . To obtain other sub-oxides, the authors have prepared a basic oxalate by mixing molecular quantities of the neutral oxalate with the oxide CdO ; the product obtained has the characteristics of a basic salt and not of a mixture. When heated in a tube closed at one extremity it decomposes, as shown by the analysis of the gases given off and of the residue, according to the following equation:— $3(\text{C}_2\text{O}_4\text{Cd} + \text{CdO}) = 2\text{Cd}_3\text{O}_2 + 5\text{CO}_2 + \text{CO}$. Cd_3O_2 is a deep green coloured powder; dilute hydrochloric acid dissolves it with the deposition of metallic cadmium, $\text{Cd}_3\text{O}_2 + 4\text{HCl} = 2\text{CdCl}_2 + 2\text{H}_2\text{O} + \text{Cd}$. It is not a mixture of CdO and Cd , as when shaken up with mercury it does not give up a trace of cadmium; it may be looked upon as a compound of CdO with Cd_2O . When heated away from

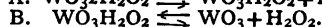
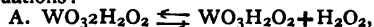
the air it decomposes into CdO and Cd; in the presence of water it decomposes rapidly into Cd(OH)₂ and Cd. By mixing 2 molecules of the neutral oxalate of Cd with 1 molecule of CdO, the authors obtained another basic salt; at least, this appears to be probable. This salt is destroyed by heat, and leaves as a residue a green powder resembling the sub-oxide, Cd₃O₂, but the analysis of the gases given off, and of the residue, shows that the reaction takes place according to the equation—



Treated with dilute hydrochloric acid, Cd₃O₂ leaves a deposit of Cd, more considerable than the oxide, Cd₃O₂:—
Cd₃O₂ + 2HCl = CdCl₂ + H₂O + Cd. The authors have made a thermochemical examination of these sub-oxides.—
Journ. Soc. Phys. Chim. R., vol. xxxiv., p. 495.

Contribution to the Study of the Inert portion of the Atmosphere.—A. Lidof.—The author estimates the nitrogen in the air by the method of direct absorption already described (*Bull. Soc. Chim.*, vol. xxi., p. 862). From a large number of determinations he arrives at the following conclusions:—1. The composition of the inert portion of the atmosphere undergoes variations which, in certain exceptional cases, may reach 7 or 8 per cent by volume. 2. The most marked and unexpected variations are met with in the autumn. 3. When the soil is frozen, so that there is no longer any exchange between the atmospheric air and that entangled in the soil, the composition of the air remains much more constant. 4. Sometimes an amount of nitrogen is found much higher than the normal, reaching 80 per cent, and this cannot be explained by errors of analysis; it must be admitted that a compound of nitrogen is present in the air, and that it decomposes, giving up nitrogen, by the action of magnesium at a high temperature.—*Journ. Soc. Phys. Chim. R.*, xxxiv., 445.

Hypertungstic, Hyperuranic, and Hypervanadic Acids.—L. Pissarjevsky.—By the examination of solutions of tungstic acid containing H₂O₂ in the presence of ether, the author found that, besides the hypertungstic acid, WO₃H₂O₂, there is another, WO₃2H₂O₂, and that by dissolution these acids are dissociated, losing H₂O₂ according to the equations:—



With a large excess of H₂O₂, the equilibrium A only takes place; if the concentration of the H₂O₂ is less, we have the equilibrium B. The Na salt of hyperuranic acid, (Na₂O₂)UO₄, dissociates in aqueous solution, forming H₂O₂. The dissolution of vanadic anhydride, V₂O₅ in H₂O₂ forms a hypervanadic acid, HVO₄, which behaves as a strong acid. All the hyperacids which by the action of sulphuric acid form H₂O₂, may be considered as having the following constitutions:—VO₂(O₂H), hypervanadic acid; WO₂(OH)(O₂H), WO₂(O₂H)₂, hypertungstic acids; MoO₂(OH)(O₂H), MoO₂(O₂H)₂, hypermolybdic acids; UO₂(OH)(O₂H), hyperuranic acid; we might even regard them as H₂O₂ in which one H is replaced by a radical VO₂, UO₂(OH), &c.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 472.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8. "Microscopic Re-solution," by Prof. J. D. Everett, F.R.S. "The Mouth Parts in the Nemocera, and their Relation to the other Families in Diptera," by Walter Wesché.

Chemical, 5.30. "Constitution of Ethyl Cyanacetate—Condensation of Ethyl Cyanacetate with its Enolic Form," by P. Remfry and J. F. Thorpe. "The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic," by W. T. Cooke. "The Union of Carbon Monoxide and Oxygen, and the Drying of Gases by Cooling," by A. F. Girvan. "Note on a Double Chloride of Molybdenum and Potassium," by G. G. Henderson. "Simplification of Zeisel's Method for the Determination of Methoxy- and Ethoxy-groups," by W. H. Perkin, sen. "The Action of Benzamidine on Olefine β-Diketones," by S. Ruhemann.

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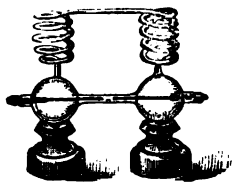
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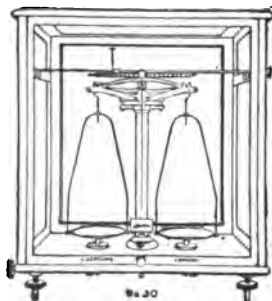
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2295.

RADIO-ACTIVE SUBSTANCES.*

By M^{me}. SKLODOWSKA CURIE.

(Continued from p. 236).

CHAPTER IV. (continued). *Theory of Radio-activity.*

THE following is, according to MM. Curie and Debierne, a very general theory which allows of the co-ordination of the results of the investigation of induced radio-activity, which results I have just stated, and which constitute facts apart from any hypothesis.

It may be said that each atom of radium acts as a constant and continuous source of energy, without actually defining the origin of this energy. The radio-active energy which accumulates in the radium tends to become dissipated in two different ways:—(1) By radiation (rays both charged and uncharged with electricity); (2) by conduction, *i.e.*, by gradual transmission to surrounding bodies in a medium of gases and liquids (production of an emanation and transformation into induced radio-activity).

The loss of radio-active energy, both by radiation and by conduction, increases with the amount of energy accumulated in the radio-active body. The system is necessarily in equilibrium when the double loss of which I have just made mention compensates the constant gain due to the action of radium. This manner of regarding the subject is similar to that in use for calorific phenomena. If in the interior of any body there is, owing to any cause a continuous and constant evolution of heat, the heat accumulates in the body and the temperature rises until the loss of heat by radiation and conduction is in equilibrium with the constant gain of heat.

In general, except under certain special circumstances, the activity is not propagated through solid bodies. When a solution is kept in a sealed tube, the loss by radiation alone takes place, and the radiating activity of the solution is of a higher degree.

If, on the contrary, the solution stands in an open vessel, the loss of activity by conduction becomes considerable, and when the state of equilibrium is attained, the radiating activity of the solution is very feeble.

The radiating activity of a solid radium salt left exposed to the air does not sensibly diminish, because the propagation of activity by conduction not taking place through solid bodies, it is a very thin superficial layer only that produces induced radio-activity. The solution, however, of the same salt produces much more intense phenomena of induced radio-activity. With a solid salt the radio-active energy accumulates in the salt, and is dissipated chiefly by radiation. On the other hand, when the salt has been for several days in aqueous solution, the radio-active energy is divided between the salt and the water, and if separated by distillation the water carries with it a large portion of the activity, and the solid salt is much less active (ten or fifteen times) than before solution. Afterwards the solid salt gradually regains its original activity.

The preceding theory may be yet further defined by supposing the radio-activity of radium itself to be produced through the medium of the radio-active energy emitted in the form of an emanation.

Each atom of radium may be considered as a constant and continuous source of emanation. At the same moment that this form of energy is produced, it undergoes a progressive transformation into radio-active energy of the

Becquerel radiation. The velocity of this transformation is proportional to the quantity of the emanation accumulated.

When a radium solution is placed within an enclosure, the emanation is able to expand into the enclosure and to spread out over the walls. Here it is, therefore, that it is transformed into a radiation, the solution giving off but few Becquerel rays; the radiation is, in some sort, *externalised*. On the other hand, with solid radium, the emanation not being able to escape readily, accumulates, and is transformed into the Becquerel radiation on the spot; this radiation therefore acquires a higher value.

If this theory of radio-activity were general, we should have to say that all radio-active bodies give rise to an emanation. Now this emission has been confirmed in the case of radium, thorium, and actinium; with the latter in particular the emission is enormous, even in the solid state. Uranium and polonium do not seem to emit any emanation, though they generate Becquerel rays. These bodies produce no induced radio-activity in an enclosed space, as do the radio-active bodies mentioned before. This fact is not in absolute contradiction to the preceding theory. If uranium and polonium were to emit emanations which become destroyed with very great rapidity, it would be very difficult to observe the carriage of such emanations by the air and the effects of induced radio-activity produced by them upon neighbouring bodies. Such a hypothesis is not improbable, since the times required for certain quantities of the emanations of radium and thorium to diminish to one-half are in the proportion of 5000 to 1. We shall see, moreover, that, under certain conditions, uranium can excite induced activity.

Another Form of Induced Radio-activity.

According to the law of dissipation in the open air of the activity induced by radium in solid bodies, the activity after one day is almost imperceptible.

Certain bodies, however, form exceptions; such as celluloid, paraffin, caoutchouc, &c. When these bodies have been acted upon to a sufficient degree, they lose their activity more slowly than the law can account for, and it is often fifteen or twenty days before the activity becomes imperceptible. These bodies appear to have the property of becoming charged with radio-active energy in the form of an emanation; they afterwards lose it gradually, causing induced radio-activity in the vicinity.

Induced Radio-activity with Slow Dissipation.

There is yet another form of induced radio-activity, which appears to be produced in all bodies which have been kept for months in an active enclosure. When these bodies are removed from the enclosure their activity at first diminishes to a very low value according to the ordinary law (diminution to one-half in half-an-hour); but when the activity has fallen to about 1/20,000 of the initial value, it diminishes no further, or at least it is dissipated very slowly, sometimes even increasing in amount. We have sheets of copper, aluminium, and glass which still retain a residual activity after six months.

These phenomena of induced radio-activity appear to be of a different kind from the ordinary ones, and show a much slower process of evolution.

A considerable time is also necessary both for the production and dissipation of this form of induced radio-activity.

Radio-activity Induced upon Substances in Solution with Radium.

When a radio-active ore containing radium is treated, with the object of extracting the radium, chemical separations are effected, after which the radio-activity is confined entirely to one of the products. In this way active products, which may be several hundred times as active as uranium, are separated from totally inactive products, such as copper, antimony, arsenic, &c. Certain other bodies (iron, lead) were never separated in an entirely inactive state. As

* Thesis presented to the Faculté des Sciences de Paris.

these active bodies are concentrated, the case is no longer the same; each chemical separation no longer furnishes absolutely inactive products; all the resulting products of a separation are active in varying degrees.

After the discovery of induced radio-activity, M. Giesel was the first to attempt to excite activity in ordinary inactive bismuth by keeping it in solution with very active radium. He thus obtained radio-active bismuth, and from this he concluded that the polonium extracted from pitchblende was probably bismuth made active by the vicinity of the radium contained in the pitchblende.

I have also prepared active bismuth by keeping bismuth in solution with a very active radium salt.

The difficulties of this experiment consist in the extreme precautions which must be taken to remove all traces of radium from the solution. If we realise what an infinitesimal quantity of radium suffices to produce very considerable radio-activity in 1 grm. of material, it is difficult to believe in the possibility of sufficiently washing and purifying the active product. Each purification causes a diminution of activity of the product, whether this be due to removal of traces of radium or that the induced radio-activity is, under these circumstances, not proof against chemical reactions.

The results I obtained appear, however, to establish with certainty the fact that the activity is produced and persists after the radium is removed. On fractionating the nitrate of my active bismuth by precipitation with water from the nitric acid solution, I found that after careful purifying it fractionated like polonium, the most active portion being precipitated first.

If the purification is not complete the opposite occurs, showing that traces of radium still remain. I thus obtained active bismuth which from the manner of fractionation showed great purity and which was 2000 times as active as uranium. This bismuth diminishes in activity with lapse of time. But another portion of the same product, prepared with the same precautions, and fractionating in the same manner, preserves its activity without diminution for actually a period of about three years.

This activity is 150 times as great as that of uranium.

I have also prepared active lead and silver by leaving them in solution with radium. Generally induced radio-activity obtained in this way scarcely lessens with lapse of time, but it does not as a rule withstand many successive chemical changes of the active body.

M. Debiere made active barium by placing it in solution with actinium. This barium remains active after several chemical reactions, its activity being therefore a somewhat stable atomic property. Active barium chloride fractionates like barium-radium chloride, the more active portions being the least soluble in water and dilute hydrochloric acid. The dry chloride is spontaneously luminous; its Becquerel radiation is similar to that of barium-radium chloride. M. Debiere has prepared an active barium chloride 1000 times as active as uranium. This barium, however, had not acquired all the characteristics of radium, for it showed none of the strongest radium lines in the spectroscopy. Further, its activity diminished on standing, and after three weeks it had become one-third of its original value.

There is a wide field for research upon the radio-activity induced in substances in solution with active bodies. It appears that, according to the conditions of experiment, more or less stable forms of induced atomic radio-activity may be obtained. The radio-activity induced under these circumstances is perhaps identical with that form, which dissipates slowly, obtained by prolonged exposure at a distance in an active enclosure. We have reason to enquire to what degree induced radio-activity affects the chemical nature of the atom, and if it is able to modify the chemical properties of the latter, either temporarily or permanently.

The chemical investigation of bodies excited at a distance is rendered difficult by the fact that the induced activity is limited to a very thin superficial layer, and that,

consequently, only a very small proportion of the material has been affected.

Induced radio-activity also results from leaving certain substances in solution with uranium. The experiment succeeded in the case of barium. If, as was done by M. Debiere, sulphuric acid be added to a solution containing uranium and barium, the precipitate of barium sulphate acquires radio-activity, and, at the same time, the uranium salts lose part of its activity. M. Becquerel found, after repeating this experiment several times, that almost inactive uranium was obtained. This might lead to the opinion that a radio-active body differing from uranium had been separated from the latter, its presence producing radio-activity in uranium. This, however, is not the case, for after some months the uranium regains its original activity; the precipitated barium sulphate, on the contrary, loses what it acquired.

A similar phenomenon is observed with thorium. Mr. Rutherford precipitated a solution of a salt of thorium with ammonia; he separated off the solution and evaporated it to dryness. He thus obtained a small very active residue, and the precipitated thorium was observed to be less active than before. This active residue, to which Mr. Rutherford gives the name of *thorium X*, loses its activity after a time, whilst the thorium regains its original activity.

It appears, then, that concerning induced radio-activity all bodies do not behave in a similar manner, and that certain of them are much more readily excited than others.

Dissemination of Radio-active Particles and Induced Radio-activity of the Laboratory.

In making investigations of strongly radio-active bodies, particular precautions must be observed for obtaining delicate determinations. The different objects used in the chemical laboratory and those used for physical experiments soon acquire radio-activity, and act upon photographic plates through black paper. Dust particles, the air of the room, clothing, all become radio-active. The air of the room becomes a conductor. In our laboratory the evil has become acute, and we no longer have any apparatus properly insulated.

Special precautions must therefore be taken to avoid as much as possible the dissemination of active dust particles, and to avoid also the phenomena of induced activity.

The objects employed in chemistry should never be brought into the room where physical research is carried on, and as far as possible should be avoided any unnecessary keeping of active substances in this room. Before beginning our researches we were in the habit, in the case of electrical experiments, of making a connection between the different parts of the apparatus by insulated metallic wires, protected by metal cylinders connected to earth, which screened the wires from all outside electrical forces. In the investigation of radio-active bodies this arrangement is quite defective; the air being a conductor there is incomplete insulation between the thread and the cylinder, and the inevitable electromotive force of contact between the thread and the cylinder tends to produce a current through the air, and to cause a deflection of the electrometer. We now screen all the wires from the air by placing them inside cylinders filled with paraffin or other insulating material. It would also be advantageous in these investigations to make use of carefully enclosed electrometers.

Activity Induced Outside the Influence of Radio-active Substances.

Attempts were made to produce induced radio-activity outside the action of radio-active bodies.

M. Villard subjected to the action of the cathode rays a piece of bismuth placed as anticathode in a Crookes tube; the bismuth was thus rendered active to a very slight degree, for it required an exposure of eight days to obtain a photographic impression.

Mr. MacLennan has exposed different salts to the action of cathode rays, afterwards warming them slightly. The salts then acquired the property of neutralising bodies positively charged.

Studies of this kind are of great interest. If, by using known physical agents, it were possible to create a considerable radio-activity in bodies originally inactive, we might hope thence to discover the cause of the spontaneous radio-activity of certain substances.

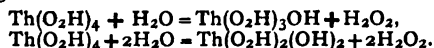
(To be continued).

ACTION OF PEROXIDE OF HYDROGEN AND HYPOCHLORITE OF SODIUM ON THE OXIDES OF THORIUM, ZIRCONIUM, AND CERIUM.

By L. PISSARJEVSKY.

By the action of a 30 per cent solution of peroxide of hydrogen on a concentrated solution of $\text{Th}(\text{NO}_3)_4$, a gelatinous, transparent precipitate of peroxide is formed; if the solution of peroxide of hydrogen is less concentrated, the precipitate takes some time to form. At the ordinary temperature the precipitate gives off oxygen, but at 0° it remains unchanged for a long time. It does not retain any NO_2H ; dilute sulphuric acid decomposes it, and liberates peroxide of hydrogen; concentrated sulphuric acid gives off ozonised oxygen. The reaction of H_2O_2 on $\text{Th}(\text{NO}_3)_4$ is never complete; it is reversible, and may be expressed by the equation $\text{Th}(\text{NO}_3)_4 + 4\text{H}_2\text{O}_2 = \text{Th}(\text{O}_2\text{H})_4 + 4\text{NO}_3\text{H}$.

$\text{Th}(\text{O}_2\text{H})_4$, which may be looked upon as the salt of the feeble monobasic acid, $\text{H}.\text{O}_2\text{H}$, becomes hydrolysed, giving:—



$\text{Th}(\text{O}_2\text{H})_2(\text{OH})_2$, when washed on a filter, is also partially hydrolysed, and a peroxide is obtained in which the proportion of ThO_2 to active oxygen is as 1 : 1.35, instead of as 1 : 1.5, as required by the formula Th_2O_7 , which has been attributed to peroxide of thorium; it is probable that the peroxide Th_2O_7 is simply a mixture of $\text{Th}(\text{O}_2\text{H})_2(\text{OH})_2$ and $\text{Th}(\text{O}_2\text{H})(\text{OH})_3$.

The reaction of peroxide of hydrogen on $\text{Zr}(\text{NO}_3)_4$ is analogous to the preceding reaction; we finally obtain $\text{Zr}(\text{O}_2\text{H})(\text{OH})_3$. The reaction of a 30 per cent solution of peroxide of hydrogen on a 17 per cent solution $\text{Ce}_2(\text{SO}_4)_3$ gives a gelatinous precipitate after about two hours which, when treated with sulphuric acid, gives off peroxide of hydrogen; sometimes there is a pulverulent precipitate mixed with it; this appears to be a compound of the peroxide and sulphuric acid.

The peroxides of Th, Zr, and Ce form with the same facility by the action of peroxide of hydrogen on the hydrated oxides, $\text{M}(\text{OH})_4 + \text{H}_2\text{O}_2 = \text{M}(\text{O}_2\text{H})(\text{OH})_3 + \text{H}_2\text{O}$.

The heats of neutralisation of $\text{M}(\text{OH})_4$ by H_2O_2 are:—

For $\text{Th}(\text{OH})_4$	+8.810 cal.
For $\text{Ce}(\text{OH})_4$	+2.704 "
For $\text{Zr}(\text{OH})_4$	+1.314 "

By the action of NaOCl on the oxides of Th and of Zr, we obtained the corresponding peroxides; with oxide of Ce we were able to prove the presence of peroxide in some experiments, but more often the results were negative, $\text{Th}(\text{OH})_4 + \text{NaOCl} = \text{Th}(\text{O}_2\text{H})(\text{OH})_3 + \text{NaCl}$.

The formation of the peroxides of Th and Zr is effected best by passing an electric current through an alkaline solution of NaCl containing the oxides of Th or Zr in suspension in a state of continual agitation.

At the same temperature and with the same strength of current, the proportion of ThO_2 transformed into ThO_3 does not depend on the amount of $\text{Th}(\text{OH})_4$ employed; the return of ThO_3 increases with the temperature (from 2° up

to 45°) and with the strength of the current. No quantitative experiments have been made with $\text{Zr}(\text{OH})_4$.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 483.

THE PIGMENTS OF GERANIUM AND OTHER PLANTS.

By A. B. GRIFFITHS, Ph.D., &c.

THE pigments produced by bacteria are dependent upon the nature of the media as well as upon the specific peculiarities of the organisms. These fungi are remarkable for the enormous number chemical substances (pigments, ptomaines, &c.) elaborated during their activity.

The chemical composition of certain bacterial pigments have been ascertained. *Micrococcus prodigiosus* produces a pigment which has the formula $\text{C}_{38}\text{H}_{56}\text{NO}_5$ (Griffiths, *Comptes Rendus*, cxv., 32), and *Bacillus cyanogenus* produces a blue pigment, and I agree with Erdmann that this pigment is probably triphenylrosaniline. Pyocyanine ($\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$) is the blue pigment formed by *Bacillus pyocyaneus*. *Bacterium alii* (Griffiths, *Bulletins de l'Académie Royale de Belgique*, Series 3, xxiii., p. 268) produces a green pigment which is soluble in alcohol. Several of the bacterial pigments are fluorescent, and some give rise to phosphorescence.

The higher fungi also form a variety of pigments, and Zopf has investigated several of them. He has proved that many fungi contain one or several different lipochromes, and he considers that these substances function as reserves. In addition to the lipochromes, the higher fungi contain a large number of other pigments. Among these is the pigment ($\text{C}_{29}\text{H}_{20}\text{O}_{10}$) (Griffiths, *Comptes Rendus*, cxxx., p. 42) of *Amanita muscaria*, which contains no nitrogen in its molecule, and also the chromophyll of the geranium which is described in this paper.

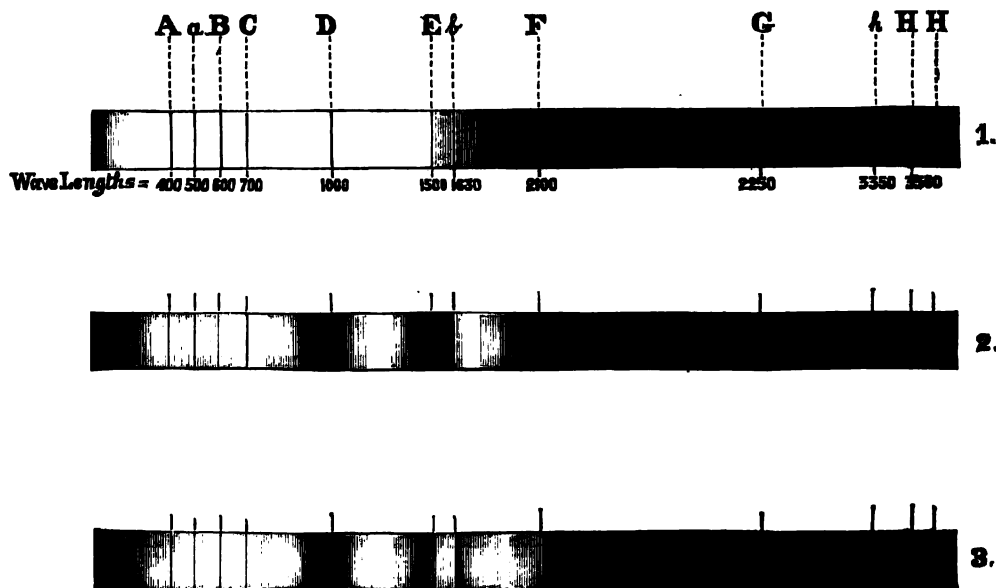
In Algae there are a variety of pigments: chlorophylls, lipochromes, phycoerythrin, &c. Phycoerythrin is probably a proteid, and according to Kerner and others may have a respiratory function.

The phanerogams contain chlorophylls (Gautier, "Chimie Biologique," p. 19; Etard, *Comptes Rendus*, cxx.), and many known and unknown pigments of great beauty. Among these pigments are two series, viz., the lipochromes and the anthocyanins. The latter occur dissolved in the cell-sap, and vary in colour from blue to red. As a rule, these pigments are soluble in water (e.g., the pigment of beet-root, &c.), and alkalis (NaOH , NH_4OH) change their colour from red to blue, and finally they become colourless. The chemistry and physics of the anthocyanins have not been fully investigated, but it is more than probable that they are derivatives of tannic acid produced by oxidation. As tannic acid is generally looked upon as a waste product, it may be that the anthocyanins belong to the same class of substances. Anthocyanins are present in the petals of blue-bells, roses, and other flowers, and in such fruits as grapes, apples, &c. The great variation in the colours of anthocyanins is due, in the first instance, to the chemical action of the living cell (e.g., such actions as acidity, alkalinity, &c., account for much that occurs in the cells of plants). The living cell produces numerous anthocyanins, all different in their chemical constitution, but still belonging to the same group or class of pigments.

The lipochromes vary from yellow to red, and are present in such fruits as tomatoes,* melons, &c., and in such flowers as daffodils, lilies, &c. It is probable that the different lipochromes of flowers and fruits have been formed from the pigments associated with chlorophyll.

The pigments to be described in this paper are crystalline substances possessing the characteristic colours of the flowers from which they came, and are odourless. These

* According to Husemann (*Liebig's Ann.*, cxvii., p. 200) carotin has the formula $\text{C}_{40}\text{H}_{56}\text{O}$.



SPECTRA OF FLOWER PIGMENTS.

1. Helianthus.

2. Geranium.

3. Verbena.

pigments may be preserved in sealed tubes, and when analysed they were found to contain carbon, hydrogen, oxygen, nitrogen, and sulphur. The pigment of geranium, however, contains no nitrogen or sulphur.

The flowers (petals) of geranium, helianthus, and verbena (red) were macerated in alcohol (90 per cent) for several hours, then heated, filtered, and finally the filtrate evaporated *in vacuo*. The pigments were treated with absolute alcohol, and the solution again evaporated *in vacuo*.

Each pigment has its characteristic absorption spectrum (see Fig.), the strength of the alcoholic solution in each case being 10 per cent and 1 c.m. thick.

The pigment of the geranium contains no nitrogen in its molecule, therefore it cannot be described as a proteid, although it may be derived from such a substance. An alcoholic solution of the red pigment evaporated to dryness yielded a crystalline substance, which was then submitted to chemical investigation.

0.2162 grm. of substance yielded 0.5006 grm. of CO₂ and 0.069 grm. of H₂O.

	Found.	Calculated for C ₁₅ H ₁₀ O ₆ .
Carbon ..	62.85	62.93
Hydrogen ..	3.53	3.49
Oxygen ..	—	33.58

The red pigment has the formula C₁₅H₁₀O₆. The acetyl derivative, prepared by heating the pigment with 1 part of dry sodium acetate and 2 parts of acetic anhydride, crystallised from methyl alcohol in red needles. They melt at 125° C., and solidify on cooling without loss in weight.

The addition of potassium acetate to the boiling alcoholic solution of the pigment yielded orange coloured prisms, which were dried at 120° C. :—

0.5844 grm. yielded 0.1567 K₂SO₄ = K = 21.50 per cent.

C₁₅H₁₈O₆K₂ requires K = 21.54 per cent.

A diacetyl compound was obtained :—

1.2144 grm. yielded 0.7297 grm. C₁₅H₁₀O₅ = C₁₅H₁₀O₆ = 77.18 per cent.

C₁₅H₈O₆(C₂H₃O)₂ requires C₁₅H₁₀O₆ = 77.29 per cent.

220 grms. of flowers (petals) gave 2.8 grms. of pigment or 1.27 per cent.

The specific rotation of the alcoholic solution of the red pigment was ascertained to be—

$$[\alpha]_D = \frac{100 \times 3.2}{2 \times 2.13 \times 1.002} = -74.97^\circ.$$

The chemical composition of the pigments of helianthus and verbena have not been ascertained, but they are nitrogenous substances. The specific rotations of their alcoholic solutions have been ascertained :—

Verbena—

$$[\alpha]_D = \frac{100 \times 4.5}{2 \times 2.6112 \times 1.0032} = -85.89^\circ.$$

Helianthus—

$$[\alpha]_D = \frac{100 \times 3}{2 \times 2.52 \times 1.004} = -59.28^\circ.$$

The electrical resistances of selenium determined by the Wheatstone bridge method, and then exposed to alcoholic solutions of the pigments of helianthus, verbena, and geranium for fifteen minutes at a distance of 5 c.m., gave the following results :—

Pigments.	Resistances of selenium before exposure. Ohms.	Resistances of selenium after exposure. Ohms.
Helianthus ..	420,000	415,000
Verbena ..	340,000	290,000
Geranium..	462,000	320,000

As light, radium rays, and Röntgen rays produce a reduction of the resistance of selenium, these investigations appear to show that solutions of the pigments emit rays. Phosphorescence has been observed in many plants, and in some animals (*e.g.*, *Pyrophorus Noctilucus*); and Mr. T. A. Edison has proved that chlorophyll, curcumin (from turmeric), and daturine (from *Datura Stramonium*) give rise to phosphorescence.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extraordinary General Meeting, July 2, 1903.

Prof. TILDEN, F.R.S., President, in the Chair.

THE PRESIDENT stated that this meeting had been summoned to consider the following changes in the By-laws which had been proposed at one meeting of the Council, and considered and approved at a subsequent meeting.

It was proposed by the Treasurer, Dr. H. T. BROWN, and seconded by Professor THORPE, "That By-law I., page 13, lines 3 and 4, be altered by deleting the words 'one year.'"

The By-law at present reads:—

"...; and he shall be entitled, so long as his annual subscription be not one year in arrear, to one copy of the annual publications of the Society."

And that the Circulars in the Appendix be altered as follows:—

In Appendix No. 2, "Letter notifying the Election of a Member":—5th and 6th lines, p. 26, delete the words "the Assistant Secretary." After the words "before admission," add the words "Payment should be made direct to the Society's Bankers (either by Cheque or Post-Office Order crossed a/c 'Chemical Society.' Your remittance should be accompanied by the enclosed Form with your Name and Address filled in."

In No. 3, "Annual Circular Letter of Treasurer":—Delete from "If paid" to end of circular, and substitute the same words as added in No. 2.

In No. 4, "Annual Circular Letter of the Treasurer to Fellows who are Two Years in Arrear of their Subscriptions":—Delete from "Payments should be made" to end of circular, and substitute the same words as added in No. 2.

The motion, having been submitted to the meeting, was declared by the President to have been carried unanimously.

The following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:—

112. "The Composition of so-called Elaeomargaric Acid." By T. KAMETARA.

Maquenne having recently shown that the composition of Cloëz's elaeomargaric acid is more closely expressed by $C_{18}H_{30}O_2$ than by the formula $C_{17}H_{30}O_2$ adopted by Cloëz, the author adduces evidence from his own work on the oil of *Elaeococca vernicia* to show that the true formula for the acid is $C_{18}H_{32}O_2$. This proof depends on the formation of the bromine additive product, $C_{18}H_{32}O_2Br_4$, and on the result of the oxidation of the acid by permanganate, the product consisting of sativic acid, $C_{18}H_{32}(OH)_4O_2$, and a small amount of another hydroxy-acid, apparently dihydroxystearic acid. Titrations with standard caustic alkali and baryta solutions give, as a mean result, 280.5 for the molecular weight of elaeomargaric acid, whilst $C_{18}H_{32}O_2$ requires 280.

113. "Phosphoric Amidines." By R. M. CAVEN.
Phenyl-*p*-tolylphosphoric amidine,—



which is formed as a by-product in preparing anilino-*p*-toluidinophosphoryl chloride (*Trans.*, 1902, lxxi., 1369), is identical with a compound obtained in the preparation of *p*-toluidinoanilinophosphoryl chloride, and which should accordingly have the formula $C_6H_4(CH_3) \cdot NH \cdot PO \cdot N \cdot C_6H_5$. This identity is not to be attributed to the mobility of a

hydrogen atom (compare von Pechmann, *Ber.*, 1895, xviii., 869 and 2362), but to the fact that the disubstituted phosphoryl chloride, in whichever way prepared, is one and the same substance, and that the derived amidine, whether a single substance or a mixture, results from the withdrawal of hydrogen chloride by the action of the substituting base.

Diphenylphosphoric amidine, $C_6H_5NH \cdot PO \cdot N \cdot C_6H_5$, and di-*p*-tolylphosphoric amidine were prepared from dianilino- and di-*p*-toluidinophosphoryl chlorides respectively.

The formation of such amidines from the diarylamino-phosphoryl chlorides by the elimination of hydrogen chloride is facilitated by the agency of basic oxides such as those of silver, mercury, and magnesium.

114. "The Mechanism of Combustion." By H. E. ARMSTRONG.

Assuming that chemical interchange and electrolysis are interchangeable equivalent terms, the author regards oxidation as an indirect process, inasmuch as the oxygen used is only indirectly incorporated with the oxidised matter; the oxidation takes place in a circuit composed of the oxidisable substance, conducting water, and oxygen; the last of these acting as the depolariser. The results obtained by Bone and Wheeler are discussed in the light of this hypothesis. It is contended that in the case of methane, for example, oxygen is introduced atom by atom, and that a substance such as carbon monoxide is a secondary product, not a direct product of oxidation nor of preferential oxidation of the carbon.

115. "The Constituents of the Volatile Oil of the Bark of Cinnamomum pedatinervium of Fiji." By E. GOULDING.

The bark of *Cinnamomum pedatinervium*, a tree indigenous to Fiji, on distillation with steam, yields nearly 1 per cent of a volatile oil which is almost colourless when first distilled, but gradually assumes a yellowish brown colour. This oil has a sweet aromatic odour, a pungent spicy taste, sp. gr. 0.964 at 15°/15°, $[n]_D^{20}$ -4.96° and n_D^{20} 1.4963. Its chief constituents are:—(i.) *A terpene*, $C_{10}H_{16}$, which has a sp. gr. 0.8659 at 15°/15°, $[a]_D^{20}$ -17.72°, and yields an uncrystallisable dibromide, $C_{10}H_{16}Br_2$; (ii.) linalool; (iii.) safrole; (iv.) eugenol; and probably (v.) eugenol methyl ether. The quantitative composition of the oil is approximately as follows:—Terpene, 15—20 per cent; alcohols, 30 per cent; esters, 1.5 per cent; safrole, 40—50 per cent; eugenol, 1 per cent; and 3 per cent of eugenol methyl ether (?).

116. "Condensation of Phenols with Esters of Unsaturated Acids." Part VIII. By S. RUHEMANN.

The compounds formed from *a*-naphthol and ethyl chlorofumarate must be formulated as derivatives of *a*-naphthaketocoumaran (compare *Trans.*, 1902, lxxxi., 419), because although guaiacol reacts with ethyl chlorofumarate to yield only ethyl guaiacoloxymumarate, yet its isomeride, the monomethyl ether of resorcinol, condenses with the ester to furnish ethyl *m*-methoxyphenoxyfumarate and an orange-coloured ketocoumaran derivative, which is called *dimethoxybisbenzaronyl*.

The latter derivative has properties similar to those recorded for bisnaphtharonyl; both compounds are reduced to colourless ketocoumaran derivatives by zinc dust and acetic acid, these reduction products being readily oxidised and converted into red substances.

Ethyl phenylpropionate, when condensed with the monomethyl ether of resorcinol, yields ethyl *m*-methoxy- β -phenoxycinnamate, the free acid of which loses carbon dioxide on heating and furnishes *m*-methoxyphenoxy-styrene.

The diethyl ether of phloroglucinol reacts with ethyl chlorofumarate to form ethyl diethoxyphenoxyfumarate, and with ethyl phenylpropionate to yield ethyl diethoxyphenoxy-cinnamate.

117. "Action of Phosphorus Trichloride on the Aromatic Ethers of Glycerol." Part II. By D. R. BOYD.

The study of the action of phosphorus trichloride on glycerol diaryl ethers has been extended (*Trans.*, 1901,

lxxix., 1221), and the following substances have been prepared:—*Glycerol, di-o-tolyl ether (d-hydroxy- α -di-o-tolylxypropane)* boiling at 226° under 13 m.m. pressure and melting at $36-37^{\circ}$; the corresponding meta-compound boiling at 232° (13 m.m.); *bisdi-o-tolylxyisopropyl phosphite* and its para-isomeride, which melt at $118-119^{\circ}$ and $81-82^{\circ}$ respectively; *di-o-* and *di-m-tolylxyisopropyl-phosphorous acids* melting respectively at $88-89^{\circ}$ and $85-87^{\circ}$, and certain of their metallic salts.

118. "Attempts to Prepare Isomeric Quaternary Salts." By M. BARROWCLIFF and F. S. KIPPING.

In view of the probable existence of isomeric salts of the type $R_1 > NR_2R_3R_4$ (*Trans.*, 1903, lxxxiii., 873), the authors have investigated some compounds of this class, including certain salts of the ethyl-propylpiperidinium base already studied by Miss C. de Brereton Evans (*Trans.*, 1897, lxi., 522); but although in all cases one of the radicles consisted of an optically active group, no indication whatever of the existence of isomerides has been observed.

Ethylpropylpiperidinium d-bromocamphorsulphonate, $C_5H_{10}NEtPr \cdot SO_3 \cdot C_{10}H_{14}BrO$, crystallises in needles melting at 211° ; it is very readily soluble in water and chloroform, sparingly so in ethyl acetate, and insoluble in ether and light petroleum. *Benzylmethylpiperidinium d-bromocamphorsulphonate*, $C_5H_{10}NMeBz \cdot SO_3 \cdot C_{10}H_{14}BrO$, melts at 166° when anhydrous, and generally resembles the preceding compound. *Ethylpiperidine d-bromocamphorsulphonate*, $C_5H_{10}NEt \cdot C_{10}H_{14}BrO \cdot SO_3H$, crystallises in needles melting at 158° .

These three salts, when repeatedly crystallised fractionally from various solvents under different conditions, did not yield dissimilar fractions. Molecular weight determinations made with ethylpropylpiperidinium iodide seem to show that whereas in aqueous solution the salt is ionically dissociated in a normal manner, yet in chloroform solution it is associated, possibly forming trimolecular complexes.

119. "Some Salts of *d-* and *l-a*-Phenylethylamines." By A. E. HUNTER and F. S. KIPPING.

The authors have investigated several salts of the *d-* and *l-*components of *dl*-phenylethylamine in the hope of obtaining isomerides corresponding with those derived from hydrindamine, but without success.

When the *d-bromocamphorsulphonate* of the *dl*-base is fractionally crystallised from water, it affords a salt which separates in prisms melting at $206-207^{\circ}$, and having in aqueous solution a molecular rotation identical with that of the *d-bromo-acid*, namely, $[M]_D + 27.1^{\circ}$; this salt, however, is not partially racemic, as might be inferred from its optical properties, but is the compound of the *l*-base; the salt of the *d*-base was not isolated.

Although the ion of the *l*-base appears to be devoid of optical activity, the free base is distinctly levorotatory in aqueous alcoholic solution, its specific rotation being about $[\alpha]_D - 25^{\circ}$; this behaviour is similar to that of the *d-* and *l*-hydrindamines.

The *benzoyl* derivative, prepared from *l-a*-phenylethylamine by the Schotten-Baumann method, melts at 120° , is optically inactive, and seems to be identical with that of the *dl*-base.

l-a-Phenylethylamine d-chlorocamphorsulphonate melts at about 198° , and has in aqueous solution a molecular rotation practically identical with that of the *d-chloro-acid*, namely, $[M]_D + 186^{\circ}$.

l-a-Phenylethylamine d-camphorsulphonate melts at $149-150^{\circ}$, and is practically indistinguishable by polarimetric examination from the corresponding salt of the *dl*-base, both substances having a molecular rotation approximating very closely to that of the acid; apparently the salt of the *dl*-base is not a definite partially racemic substance.

120. " *β -Bromocinnamic Acids.*" By J. J. SUDBOROUGH and K. J. THOMPSON.

Small amounts of *β -bromoallocinnamic acid* (m. p. $159-160^{\circ}$) are obtained by the action of alkalis on cinnamic acid dibromide, but are not produced when the ethyl ester is used instead of the free acid dibromide.

In aqueous solution, the products of the combination of hydrogen bromide and phenylpropionic acids consist entirely of *β -bromo-* and *β -bromoallo-cinnamic acids*; the relative amounts of the two isomerides being but slightly affected by light, temperature, or concentration of the solvent. The nature of the combination is materially affected by the medium in which the hydrogen bromide is dissolved; when acetic acid is used, more of the *β -bromo-acid* and less of the *β -bromoallo-acid* are obtained than when saturated aqueous solutions are employed. With benzene and carbon disulphide, the chief product is *α -bromo-cinnamic acid*.

Similar results have been met with in the combination of ethyl phenylpropionate and hydrogen bromide.

Under the influence of alkalis, *β -bromocinnamic acid* and its esters lose hydrogen bromide much more readily than the *β -bromoallo-acid* and its esters.

Attempts have been made to prepare Michael's *iso-cinnamic acid* in order to determine whether either the *allo-* or the *iso-acid* could be resolved into optically active constituents by the aid of active bases. The experiments made on the reduction of the *β -bromoallo-acid* indicate that the product, which consists of *allocinnamic acid* with a trace of ordinary cinnamic acid, does not contain the *iso-acid*.

121. "Vapour Pressure of Aqueous Ammonia Solution." Part II. By E. P. PERMAN.

The partial pressures of the ammonia and water-vapour evolved by an aqueous ammonia solution have been found by aspirating a known volume of air through the solution, and estimating the amounts of ammonia and water withdrawn. The experiments were made at temperatures ranging from 0° to 60° , and the concentration of the solutions employed varied from 0 to 22.5 per cent of ammonia.

It was found that the sum of the partial pressures was equal to the total pressure determined by the statical method, and also that the relationship between the partial pressures and the concentration of the solution is that deduced by Duhem and others for binary mixtures of liquids.

122. "Isomeric Aminoamidines of the Naphthalene Series." (Fourth communication on Anhydro-bases). By R. MELDOLA, J. V. EYRE, and J. H. LANE.

The authors have succeeded in isolating the free base, ethenyltriaminonaphthalene, obtained by the reduction of dinitro-*a*-acetophthalide by tin and hydrochloric acid. The compound is characterised by its tendency to form complex hydrates containing $9\frac{1}{2}$, $3\frac{1}{2}$, or $1\frac{1}{2}$ mols. of water. The *acetate*, $C_{12}H_{11}N_3 \cdot C_2H_3O_2 \cdot H_2O$, *oxalate*, $C_{12}H_{11}N_3 \cdot C_2H_3O_4 \cdot 2H_2O$, and *mercurichloride*,—



have been prepared.

The *N*-ethyl derivative of the acetyl derivative having the formula $C_{16}H_{17}ON_3 \cdot \frac{1}{2}H_2O$ has been obtained, and characterised by the formation of its *picrate*, $C_{16}H_{17}ON_3 \cdot C_6H_4(NO_2)_3OH \cdot H_2O$, and *aureichloride*, $C_{16}H_{17}ON_3 \cdot HAuCl_4 \cdot 2H_2O$.

By eliminating the NH_2 group in the ethenyltriaminonaphthalene by the diazo-method, an ethenyldiaminonaphthalene (methylnaphthimidazole) has been obtained, which differs from the only compound of this formula at present known (Prager, *Ber.*, 1885, xviii., 2161). The isomerism of the aminoamidines has thus been proved to extend to the parent compounds, so that the cause of the isomerism is to be sought in the structure of the amidine ring. The following salts and derivatives have been prepared:—*Hydrochloride*, $C_{12}H_{10}N_2 \cdot HCl \cdot H_2O$, *chromate*, $C_{12}H_{10}N_2 \cdot H_2CrO_4 \cdot 2H_2O$, and *picrate*.

The base itself has the formula $C_{12}H_{10}N_2 \cdot H_2O$, and the

water could not be expelled without decomposing the compound. The amidine ring apparently breaks down by the action of benzoyl chloride in presence of alkali with the formation of dibenzoyl-*o*-naphthylenediamine. The *N*-menthyl derivative, an oily base, has a crystalline *picrate*, $C_{13}H_{12}N_2 \cdot C_6H_5(NO_2)_3O_2H$. The crystalline *N*-ethyl derivative, $C_{14}H_{14}N_2$, is anhydrous, and yields the following crystalline salts:—*Chromate*, $C_{14}H_{14}N_2 \cdot H_2CrO_4$, and *picrate*, $C_{14}H_{14}N_2 \cdot C_6H_5(NO_2)_3O_2H \cdot H_2O$; its *aurichloride* contains $2H_2O$, and, when heated in the water-oven, becomes converted into the monohydrate. The *platini chloride* also yields hydrates containing 4, 2, and 1 mols. of water.

The *N*-ethyl derivative of the known ethenyl-diamino-naphthalene (compare Otto Fischer, *Ber.*, 1901, xxxiv., 935) prepared for comparison with its isomeride, is found to be resinous, but the *chromate*, *picrate*, *platinichloride*, and *aurichloride* are well characterised.

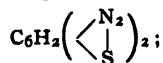
The ethenyltriaminonaphthalene, obtained by the reduction of dinitro- α -acetonaphthalide by iron and hydrochloric acid (Markfeldt's base) yields a crystalline *oxalate* with $4H_2O$ and a *mercurichloride*, $C_{12}H_{11}N_3 \cdot 2HCl \cdot HgCl_2 \cdot 5H_2O$. Its benzoyl derivative has now been prepared by the Schotten-Baumann method (compare *Trans.*, 1900, lxxvii., 1165).

Ethenyltriaminonaphthalene (Meldola and Streatfeild's base) is converted into its isomeride (Markfeldt's) by further reduction with iron and hydrochloric acid, but reduction with sodium amalgam in the presence of acetic acid does not bring about this transformation. Reduction of dinitro- α -acetonaphthalide with zinc and hydrochloric acid gives the original (M. and S.) base.

123. "Olythiosulphonic Acids of *p*-Diamines." By A. G. GREEN and A. G. PERKIN.

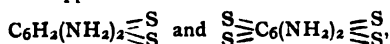
The series of polythiosulphonic acids of *p*-diamines formerly prepared by one of the authors in collaboration with A. Meyenberg (compare Eng. Pat. Specifications, 1898, Nos. 21832, 22460, 22847; 1899, Nos. 5039, 18658; and 1900, No. 4792) are well-crystallised compounds which, when oxidised together with primary amines and diamines, give rise to a series of black colouring matters possessing the characteristic properties of "sulphide" colours. The present communication deals with the further characterisation of these polythiosulphonic acids, especially of the di- and tetra-thiosulphonic acids of *p*-phenylenediamine, $C_6H_4(NH_2)_2(S \cdot SO_3H)_2$ and $C_6H_4(NH_2)_2(S \cdot SO_3H)_4$, which are obtained by the oxidation of *p*-phenylenediamine in the presence of sodium thio sulphate, using 2 or 4 molecular proportions of the latter with a corresponding quantity of the oxidising agent.

Owing to the presence of the S_2O_3H groups in ortho-positions with respect to the amino-radicles, the *p*-phenylenediaminedithiosulphonic acid exhibits several characteristic condensations. Thus, with nitrous acid it gives a stable bisdiazosulphide,—



with organic anhydrides or with aldehydes, it gives anhydro-compounds.

On boiling the di- or tetra-thiosulphonic acid with aqueous acids, sulphurous and sulphuric acids are eliminated, and yellow or red salts of sulphide bases are obtained. These bases, which appear to have the constitution—



are of dark colour, insoluble in water and other solvents, but dissolving in an aqueous solution of sodium sulphide, in which respect they resemble the "sulphide" colours; they are re-converted into the respective polythiosulphonic acids by prolonged treatment with sulphurous acid in the presence of air.

When treated with zinc dust, the dithiosulphonic acid is reduced to the disulphide, $C_6H_4(NH_2)_2(SH)_2$.

124. "The Rotation of the Menthyl Esters of the Isomeric Chlorobenzoic Acids." By J. B. COHEN and S. H. C. BRIGGS.

The authors have prepared the menthyl esters of the mono- and di-chlorobenzoic acids, and have compared their specific and molecular rotations.

The following represents the order of optical activity, beginning with the least active:—2:6; 2:3; ortho; 2:5; 2:4; 3:4; 3:5; unsubstituted; meta; para. These results lead to the following conclusions:—1. The greatest effect (decrease) in the rotation of the unsubstituted menthyl ester is produced when the halogen enters the ortho-position with respect to the carboxyl group; the least, when the halogen is in the meta- and para-positions, which, singly, slightly increase the rotation. 2. The monohalogen derivatives accord with the rule laid down by Frankland and Wharton (*Trans.*, 1896, lxxx., 1320, 1583), and confirmed by Guye and Babel (*Abstr.*, 1899, ii., 719), and Tschugaeff (*Abstr.*, 1903, ii., 2), and follow the order: ortho, unsubstituted, meta, para.

3. Two halogens attached to adjoining carbon atoms (2:3 and 3:4) produce a greater effect than either singly.

It might be expected that the rotations of the 2:3- and 2:5-esters would be approximately the same, inasmuch as the chlorine atoms in both isomerides occupy the ortho- and meta-positions with respect to the carboxyl group, but in reality the rotation of the 2:3-ester is much lower, and that of the 2:5-isomeride slightly higher than the value obtained for the ortho-compound.

The low rotation of the 3:4- and 3:5-esters does not support the theory of the lever-arm (Frankland and Wharton, *loc. cit.*).

125. "The Reaction between Phosphorus and Oxygen." Part I. By E. J. RUSSELL.

A small quantity of water is necessary for the oxidation of phosphorus, and the reaction proceeds most rapidly when that amount is present which is left after drying with sulphuric acid. In the presence of much water-vapour, action is considerably retarded. The formation of ozone and hydrogen peroxide requires the presence of excess of water; these bodies are not direct products of the reaction between phosphorus and oxygen.

Moderately dried phosphorus and oxygen react under all the pressures employed, and the phenomena of false equilibrium are not seen. The reaction may be divided into two stages:—In the first, oxidation is slow and accompanied by a very feeble glow, the action being apparently unimolecular; the oxide formed is still under investigation. The second stage begins when the pressure falls below about 500 m.m.; oxidation is continuously accelerated until all the oxygen is absorbed. The luminosity is very marked, and phosphorus pentoxide is formed. No simple expression could be found connecting the velocity of oxidation with the pressure of oxygen.

When an inert gas, such as nitrogen, is present, the phenomena are substantially the same, but the acceleration of the second period ceases after a time, and a retardation sets in. This variation is, however, explained on a purely mechanical hypothesis.

When phosphorus oxidises in moist oxygen, the reaction differs from that taking place in dry oxygen in the following respects:—

(a). It does not begin until the pressure of oxygen is less than about 500 m.m.; when it does take place it is slower, and is much retarded during the earlier part of the reaction. The retardation is explained as being due to a protective film formed by the water on the phosphorus.

(b). Ozone and hydrogen peroxide are produced, and, in presence of nitrogen, these substances are accompanied by ammonium nitrite and nitrate. None of the theories at present held completely accounts for these observations.

If smaller quantities of water are present (4 or 5 m.m. pressure instead of 16 or 20 m.m.), the velocity curve does not differ greatly from that obtained in the absence of

water. And the difference observed when the higher quantity of water is present can readily be explained as being due to the protective layer of this liquid. There is no reason to suppose that the primary reaction between the phosphorus and oxygen differs in the two cases.

126. "Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Sulphate." Part IV. By R. S. MORRELL and J. M. CROFTS.

The substances formed by adding hydrogen peroxide solutions of arabinose and rhamnose in the presence of ferrous sulphate yielded osazones with phenylhydrazine acetate, and it was therefore considered that arabinose and rhamnose had been oxidised to the corresponding osones (*Trans.*, 1889, lxxv., 786, and 1900, lxxvii., 1219). Aqueous solutions of these two osones have been found to react at the ordinary temperature with *p*-bromophenylhydrazine, giving rise to osazones. The action of larger quantities of hydrogen peroxide on glucose and fructose has been investigated, and the metallic salts of glyoxylic, glycollic, and trihydroxybutyric acids have been obtained. The formation of glycollic acid from glucose is peculiar, and is not easily accounted for on the assumption that the sugar molecule is transformed into an osone before a disruption of the carbon chain takes place.

127. "Ethyl Benzylideneanilineacetate." By R. S. MORRELL and A. E. BELLARS.

The authors find that the action of benzylideneaniline on ethyl acetoacetate gives rise to ethyl benzylideneanilineacetate, which melts between 78° and 80° after re-crystallisation from benzene and carbon tetrachloride. The addition of piperidine or minute quantities of sodium ethoxide does not cause any change in the melting-point of the re-crystallised addition product (compare Schiff, *Ber.*, 1898, xxxi., 207; Rabe, *Ibid.*, 1902, xxxv., 3950; Francis, *Ibid.*, 1902, xxxv., 3949), but the solvents used in the re-crystallisation must be pure, otherwise it is impossible to obtain the ethyl benzylideneanilineacetate with a constant melting-point. The addition of small quantities of sodium ethoxide to a mixture of benzylideneaniline and ethyl acetoacetate causes the formation of a mixture of β_1 - and β_2 -forms of ethyl benzylidenediacetate (Rabe, *Annalen*, 1900, 313, 176). The molecular weight of the ethyl benzylideneanilineacetate in benzene or carbon tetrachloride solution decreases as the solution becomes more dilute, and also on heating or when it is kept for some time.

128. "Studies on Enzyme Action. I. The Correlation of the Stereoisomeric α - and β -Glucosides with the Corresponding Glucoses." By E. F. ARMSTRONG.

The stereoisomeric α - and β -alkyl glucosides have been converted, by means of enzymes, into the corresponding glucosides. It is thus shown that glucose has a lactonic structure, and consists, in solution, of a mixture of two stereoisomeric lactones. The changes in rotatory power which dissolved glucose undergoes involves the passage of one or other form of the lactone into a mixture of the two.

129. "A Dynamical Study of the Friedel-Crafts Reaction." By B. D. STEELE.

In order to determine, if possible, the mechanism of the Friedel-Crafts reaction, the synthesis of phenyl tolyl ketone from toluene and benzoyl chloride in presence of aluminium or ferric chloride, and that of phenyltolylmethane from toluene and benzyl chloride in presence of the same condensing agents, have been studied dynamically.

The course of the reaction in each case was followed by passing a rapid current of hydrogen through the reaction mixture, and titrating the hydrochloric acid thus carried over.

The following conclusions have been deduced:—

1. In the synthesis of a ketone from a hydrocarbon and an acid chloride in the presence of aluminium chloride, the explanation suggested by Perrier (*Ber.*, 1900, xxxiii., 815) and by Boeseken (*Rec. Trav. Chim.*, 1900, xix., 19; 1901,

xx., 102) seems to be quite justifiable, providing that the aluminium chloride is not present in excess.

2. In the presence of an excess of the condensing agents, the reaction, instead of being unimolecular, becomes bimolecular, and is best explained by assuming that the reagents are two intermediate compounds, each containing aluminium chloride.

3. In the presence of ferric chloride, the reaction is also bimolecular, and is best explained on the foregoing assumption.

4. The synthesis of phenyltolylmethane from toluene and benzyl chloride, in the presence of either aluminium or ferric chloride, is a unimolecular reaction, due to the interaction of the toluene and a compound of the organic and metallic chlorides.

PHYSICAL SOCIETY.

Ordinary Meeting, November 13, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

SIR OLIVER J. LODGE read a paper on "Means for Electrifying the Atmosphere on a Large Scale."

Twenty years ago the author was engaged with Mr. J. W. Clarke on an investigation of the dark spaces seen near hot bodies placed in illuminated smoke. The existence of these dust-free spaces was discovered by Tyndall, and the phenomenon had been investigated by Lord Rayleigh. Tyndall worked with high temperatures, and attributed the effect to the burning of the dust near the hot body. Such, however, cannot be the case, as the spaces exist when inorganic dust, such as oxide of magnesium, is used. The conclusion at which Messrs. Lodge and Clark arrived (see *Phil. Mag.*, 1884) was that the result was due to an aerial bombardment from the hot wire which drove the particles away, and they tried the effect of electrifying the hot body to see if there was any modification of the dark space. A new phenomenon was discovered; the whole of the dust being driven to the sides of the containing vessel. This experiment was shown by the author at the British Association meeting in Montreal in 1884, and subsequently, on a larger scale, at the Royal Institution. In the latter experiment two pieces of wire gauze, connected to the terminals of an electric machine, were placed opposite each other in a smoke-filled chamber, through which a current of smoke was slowly passing. Upon electrifying the plates the smoke ceased passing, the dust particles cohered, hovered in the air, and were either driven to the sides of the chamber or fell to the bottom. In the case of mist, electrification of steam in a bell-jar converted it into fine rain. It seems therefore possible that rain might be produced by the electrification of a cloud. Sir Oliver Lodge has tried at Liverpool to disperse fogs by discharging electricity into them. For this purpose a large mast was erected on the roof of the University College buildings. It terminated in a bundle of points, to which electricity was conveyed from a Wimshurst machine by a wire supported by specially constructed insulators. In order to drive electricity from a point far removed from a surface a high potential is necessary, and sometimes a large gas flame was used to supplement the points. Upon one occasion the discharge of electricity from the flame was sufficient to keep a clear space of 50 or 60 yards radius in a dense fog. The author had hoped to induce the Mersey Dock Board to try the principle on a large scale, having a series of positive discharges on one side of the river and a series of negative discharges on the other; but he felt a certain reluctance in recommending the method to practical men so long as it was necessary to derive the current from a Wimshurst machine. A dynamo would be a more suitable generator if it were possible to get a sufficiently high potential. The way out of the difficulty is to rectify a high-tension alternating current, and Sir Oliver Lodge has for some time been considering the possibility of doing this by utilising Cooper-Hewitt mercury

lamps. A study of these lamps has led him to believe that their rectifying power is much assisted by the outside metallic coating which surrounds the mercury electrode, and which is connected to the positive terminal of the lamp. In order to rectify an alternating discharge, four lamps are so arranged in the form of a quadrilateral that, when the leads from the terminals of an alternating transformer are connected to two opposite corners, two unidirectional currents are obtained from the other corners. Experiments have been made at Birmingham by sending the current from a high-frequency alternator ($3000 \sim$ per sec.) through the primary of an induction coil and connecting the terminals of the secondary to the rectifiers. The length of the rectified spark can be increased by putting a number of lamps in series in each arm of the quadrilateral arrangement. Sir Oliver Lodge performed an experiment at the meeting to show the dissipation of fog by electrification. The current from an alternator was passed through the primary of a coil and the terminals of the secondary connected to the rectifiers, twelve lamps in all, three in series in each arm. This arrangement is capable of giving a rectified spark 2 or 3 inches long, the unidirectional nature of which can be proved by passing it through a Crookes or a Röntgen tube. Some magnesium wire having been burnt under a large bell-jar to fill it with a cloud of magnesium oxide, the jar was then illuminated by the light from an electric lamp. Passing through the base-piece upon which the bell-jar was placed was a conductor which terminated in a point inside the jar. When the terminals between which the rectified discharge was passing were separated and the other end of this conductor was joined to one of them, the electricity streaming from the point into the clouded atmosphere caused an immediate deposition of the magnesium oxide.

Prof. W. E. AYRTON congratulated the author, and expressed his interest in the experiment showing the deposition of magnesium oxide. He pointed out that the combination of four Nodon valves for obtaining a continuous current from an alternating one had been used before. Dealing with the rectifier itself, he said his feeling was that the rectification was due to a difference in the electrodes and not to any special proximity of two electrodes through the glass as suggested by Sir Oliver Lodge. There were many cases of rectification—a metal-carbon arc for instance. In this case the explanation of the phenomenon was probably connected with the fact that one electrode was metallic and the other carbon. In the mercury lamp both electrodes were metallic, but the metals were very different from each other. Prof. Ayrton said that Prof. Steinmetz had recently shown him some interesting experiments with mercury arc-lamps resembling in some details the Cooper-Hewitt lamp. There was, however, no choking coil, the starting being effected by an electro-magnet capable of separating two tags within the tube, and causing a small arc which started the lamp. There was also no branch lead from the positive electrode to the mercury end of the lamp. In his opinion this connection was only a starting device in the Cooper-Hewitt lamp. Prof. Ayrton concluded by expressing his pleasure that the administrative duties of Sir Oliver Lodge had not interfered with his keen interest in scientific research.

Prof. H. L. CALLENDAR expressed his interest in the paper and in the experiments shown. In connection with the rectification he pointed out that under certain conditions any vacuum-tube would act as a rectifier, illustrating the point by an experiment with an X-ray tube. The phenomenon was noticed by Hittorf thirty years ago, and attributed by him to the constriction around the negative electrode.

Mr. W. DUDELL said he should like to discuss the rectifying power of mercury lamps. Any two different electrodes in air will rectify to some extent. In the case of two carbons, the diameters of which are as two to one, the resistance between them varies by 5 or 6 per cent, according as the current is passed one way or the other. With a metal-carbon arc it is possible to stop the current altogether. A point and plate will also act as a rectifier. He thought that the condenser arrangement was to facilitate starting,

and expressed the opinion that the rectification was due to the temperature of the electrodes and the temperature gradients near them. The temperatures of the mercury and iron in a mercury lamp were very different, and in the case of a point and plane there was a difference of temperature because of the cooling of the plane by radiation. He had also found that the best rectification takes place between electrodes having a high potential difference, and that when using the lamp for practical purposes the presence of impurities improved it by facilitating starting.

Dr. C. CHREE pointed out that there was a potential gradient in the atmosphere from the ground upwards which sometimes amounted to 1000 volts per metre, and was often 150 volts per metre. He asked if this difference of potential between the ground and the tops of high trees would have any effect upon the dissipation of fog.

Sir OLIVER LODGE, replying to Dr. Chree, said it had occurred to him that atmospheric electricity must be taken into account, and said it was quite feasible that point discharges from trees might have some effect upon fogs, but not enough. Replying to Mr. Duddell, he said they had found that for high tension rectification it was necessary to have as good a vacuum as possible, but for lamps working on low voltages it was beneficial to permit a residue of impurities. He said he was still of the opinion that the outside connection assisted the rectification in some tubes by throwing a great strain on the gas near the cathode.

Sir OLIVER LODGE then described an Arrangement for Driving Mercury Pumps, designed by himself and Mr. B. Davies.

The apparatus was constructed because the work necessary to make large numbers of vacuum-tubes renders it essential to drive the pump hydraulically. The preliminary exhaustion is effected with an ordinary Fleuss pump and the work completed by using a Töpler mercury pump. The reservoir of the pump is suspended from the rim of a six-inch wheel, and is almost counterbalanced by a water-vessel suspended from the rim of a two-foot wheel fixed upon the same axle. The water-vessel is capable of moving up and down between vertical guides, and mechanism is so arranged that when it reaches the top of the guides a tap is turned, and it is filled with water. The increase in weight causes it to descend and raises the pump reservoir. When it reaches the bottom of the guides a valve in the bottom of the vessel is opened automatically and the water is discharged. The vessel then rises again, and the process is repeated. Keyed to the axle carrying the two wheels referred to, there is a third wheel, one foot in diameter, over the rim of which passes a friction band. The function of this arrangement is to control the upward and downward motion of the water-vessel, bringing it to rest quietly at each end of the journey, and yet allowing it to move quickly. There is also a device at the bottom of the guides for keeping the valve of the vessel open until the whole of the water has been discharged. The mercury which overflows from the pump is conducted back to the reservoir, thus giving a circulation of mercury and automatically replenishing the reservoir.

Reaction between Benzene and Cellulose.—A. M. Nastukof.—The author has already obtained a product of the reaction between benzene and cellulose; this product appears to be a tetraphenylised derivative of cellulose. Analysis shows the presence of sulphur; the best method of representing the results would be to consider this compound as a tetraphenylcellulose containing 2SO_2 for $6[\text{C}_6\text{H}_5\text{O}_5(\text{C}_6\text{H}_5)_4]$, and which, dried in the desiccator, has lost $9\text{H}_2\text{O}$, or which has lost $12\text{H}_2\text{O}$ when dried at $105-110^\circ$; according to the method adopted we get the formula $\text{C}_{180}\text{H}_{134}\text{O}_{25}\text{S}_2$ or $\text{C}_{180}\text{H}_{128}\text{O}_{22}\text{S}_2$. From the analyses of the products of oxidation and dry distillation, it must be admitted that the groups C_6H_5 replace the H's fixed directly to the C's, and not the H's of the OH groups.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 505.

NOTICES OF BOOKS

Introduction to Metallurgical Chemistry, for Technical Students. By J. H. STANSBIE, B.Sc. (Lond.), F.I.C., &c. With 46 Illustrations. Bristol: John Wright and Co. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1903. Pp. 200.

As a preparatory course to the study of metallurgy proper, we are glad to recommend the book now before us. It deals principally with the chemistry of the metals, though of course a certain amount of space is devoted to the other elements. Metallurgy, in the ordinary sense of the term, deals almost entirely with operations requiring the use of fire, but it is of the greatest importance that students should be well acquainted with the chemistry of the elements dealt with in metallurgical operations, and in these days of technical education and specialism such a book as the present one will be found of great assistance to those students who have decided on making metallurgy their special study.

The book is divided into twenty-five chapters, the earlier ones being devoted to the general physical and chemical properties of the elements, both metallic and non-metallic. In Chapter X. we come to what may be considered the more technical side of the subject, viz., carbon and its compounds. This chapter is followed by those on "Reduction," "Combustion," "Silicon, and its Compounds with Oxygen and Metals," &c.

Electro-chemical action also finds a place, and students would do well to pay close attention to this branch of the subject, as electricity is becoming daily more and more closely associated with metallurgical operations.

The book is well arranged and the descriptions clear, and there are a number of questions at the end of each chapter on the subjects just dealt with; we must, however, again point out a fault which is too common in books of this class, viz., the character of the illustrations. Many of them are entirely superfluous, as they illustrate simple bits of apparatus which must of necessity already be familiar to any intelligent youth who has taken any interest in chemistry or science. The book closes with an appendix and a short index of three pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

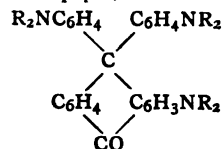
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 16, October 19, 1903.

Carbon Vapour.—M. Berthelot.—It is known that incandescent electric lamps contain a filament of amorphous carbon, obtained by calcination of vegetable matter. This thread is raised to a red heat in a vacuum by the electric current, and gives forth a trace of carbon vapour, which condenses on the bulb, forming, after a time, a brown deposit. The author investigates the state of this carbon vapourised at the lowest possible temperature, and compares it with the known allotropic forms of carbon. The result of his experiments is that the carbon vapour obtained under these conditions, i.e., at the lowest possible temperature, contains no graphite and no diamond, but only a variety of amorphous carbon. He also makes some experiments on the vapour-tension of carbon.

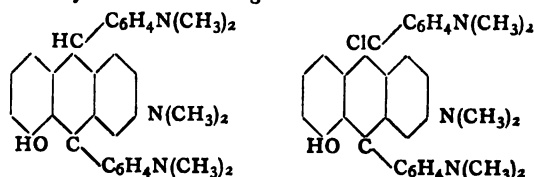
Estimation of Argon in Atmospheric Air.—Henri Moissan.—Already noticed.

Products of Condensation of Tetramethyldiamidophenylloxanthranol with Benzene, Toluene, and Dimethylaniline: Phthalic Green.—A. Haller and A.

Guyot.—The addition products of tetramethyldiamidophenylloxanthranol with benzene, toluene, and dimethylaniline are not amidodiphenylanthrones, the two tetraalcoyldiamidodiphenylanthrones which the authors have described in a previous paper, and whose constitution,—



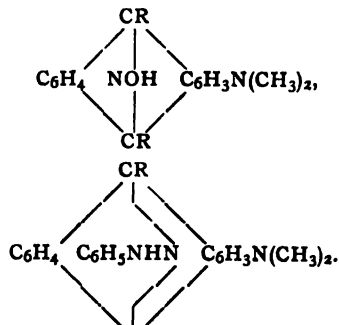
is not doubtful, are yellow in the free state, give with acids colourless salts, and do not combine with hydroxylamine or phenylhydrazine; whilst the former substances are colourless in the free state, forming with acids strongly coloured salts and combining with phenylhydrazine and hydroxylamine with loss of 2 mols. of water. A series of experiments on their constitution lead to the conclusion that they have the following formulæ:—



Leuco-derivative of phthalic green.

Phthalic green (chlorohydrate).

The combination of the bases with hydroxylamine and phenylhydrazine may be regarded in the following manner:—



R representing the radicles C_6H_5 , $C_6H_4CH_3$ and $C_6H_4N(CH_3)_2$.

Composition of Zinc Peroxide.—M. Kuriloff.—The zinc oxides prepared by M. de Forcrand show forms of intermediate oxidation, and their composition depends on the methods used to obtain them. The composition of zinc peroxide is analogous to cadmium peroxide and corresponds to the formula $Mo_2M(OH)_2$. The author asserts that this latter formula is the only one definitely established up to the present time, the other types not having been verified. After establishing the individuality of the different degrees of oxidation, it will be possible to definitely settle the question as to the characteristics of these peroxides and compare them with the peroxides of barium, strontium, and calcium.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. A. K. Huntingdon, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., J. Francis Mason, and Edward H. Woods were elected members.

Action of Bin oxide of Sodium on Paraldehyde.—L. Vanino.—Bin oxide of sodium in the form of powder, mixed with paraldehyde, oxidises it rapidly, and bursts into flame. Contrary to most of the oxidising reactions of this body, this latter one takes place by simple contact, without previous heating or the addition of water. Formic aldehyde in aqueous solution generally detonates under the influence of peroxide of sodium.—*Zeit. Anal. Chem.*, vol. xli., p. 619.

Approximate Estimation of Albuminoids.—A. Jolles.—Permanganate of potassium in slightly acid solution oxidises albuminoids. The amount of nitrogen given off by hypobromite of soda in the neutralised liquor is nearly a constant fraction of the original albuminoid. This method can be applied to the estimation of albuminoids in urine in the following manner:—Precipitate 25 or 50 c.c. of urine, at boiling temperature, by means of acetic acid in the presence of chloride of sodium. The precipitate being collected in a beaker with 300 to 400 c.c. of water, add 5 c.c. of sulphuric acid ($d = 1.4$), and boil while gradually adding permanganate up to 8 grms. per litre, until the precipitate of peroxide is constant. Dissolve the latter in oxalic acid, and concentrate to 50 c.c. Neutralise when cold with soda, then set free the nitrogen in a ureometer. The weight of nitrogen, multiplied by 7.68, represents the weight of albuminoid. The error found by comparison with the gravimetric method is about 2.5 per cent more or less.—*Zeit. Anal. Chem.*, vol. xli., p. 589.

Use of Sulphate of Hydrazine in Analysis.—E. Orlof.—Sulphate of hydrazine, while exercising its oxidising function in alkaline solution, gives off a volume of nitrogen equal to the volume of oxygen reacting: $\text{SO}_4\text{N}_2\text{H}_4\text{H}_2 + \text{O}_2 = \text{SO}_4\text{H}_2 + 2\text{H}_2\text{O} + \text{N}_2$. The author has made use of this reaction for analysis by oxidation in alkaline solution. The oxidising agent is first titrated with respect to the N given off with $\text{SO}_4\text{N}_2\text{H}_4\text{H}_2$. The substance is treated with the titrated solution of the oxidiser, and, when the reaction is terminated, $\text{SO}_4\text{N}_2\text{H}_4\text{H}_2$ is added; the number of c.c. of nitrogen given off represents the volume of oxygen not used in oxidising the substance in question. The author has used this method in the following oxidising reactions:—1. Oxidation by means of ferricyanide and KOH according to the equation $2\text{K}_3\text{FeCy}_6 + 2\text{KOH} = 2\text{K}_4\text{FeCy}_6 + \text{H}_2\text{O} + \text{O}$. 2. Oxidation by means of KMnO_4 in alkaline solution: $6\text{KMnO}_4 = 3\text{K}_2\text{O} + 2\text{Mn}_2\text{O}_4 + 13\text{O}$. 3. Oxidation by means of chloride of lime, and, in general, by means of chlorine, bromine, and iodine in alkaline solution. The methods, which will be described in detail in a future paper, are applicable to the analysis of various industrial products.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 449.

Synthesis of a New Aromatic Hydrocarbid Decacyclene (Trinaphthylenebenzene), and of a Derivative of Thiophene having a Red Colour, Dinaphthylenethiophene.—C. Dziewonski.—100 grms of acenaphthene and 23 grms. of finely powdered sulphur were thoroughly mixed and heated gently in a half litre flask. A strong reaction takes place at about 205° with the evolution of sulphuretted hydrogen, and the melted mass gradually takes a deep red colour. Towards the end of the reaction, which is known by the diminution of the volume of sulphuretted hydrogen given off, the temperature is raised to $290-294^\circ$ for a few minutes. When the reaction has become less at this temperature, which must not be exceeded, however, or there would be danger of decomposition, the whole is allowed to cool, and is treated with boiling alcohol five or six times in the endeavour to remove all the acenaphthene which has not entered into the reaction. The substance remaining is extracted with benzene, and on evaporating the latter a red body is obtained which is crystallised, mixed with animal-black, several times in toluene; in this manner a pure substance is obtained in very fine red needles. A further quantity of this red body can be extracted from the residue in the flask by treating

it with toluene. Finally, the residue, mixed with animal-black, is treated with boiling cumol, which dissolves a certain proportion; this eventually crystallises out in the form of small golden-yellow needles. The author then describes a number of the reactions of these bodies.—*Bull. Soc. Chim.*, vol. xxix., No. 9.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough.

WEDNESDAY, 25th.—Society of Arts, 8. "The Universal Exposition at St. Louis, U.S.A., 1904," by George F. Parker.

FRIDAY, 27th.—Physical, 8. (At the Royal College of Science, South Kensington). "An Electrical Thermostat," by S. Darwin. "Occurrence of Cavitation in Lubrication," by S. Skinner. "Lecture Experiment in Electrical Resonance," by Dr. W. Watson.

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Fractional Combustion of a Mixture of Methane and Hydrogen by Winkler's Method.—K. V. Charitchkof. —Experiments have been carried out on various mixtures of hydrogen and methane. It was found that at 90° the combustion of the hydrogen was complete, but there is always a certain quantity of CO₂ formed; the combustion of the methane mixed with hydrogen may be noticeable at this low temperature. In principle, the method is not applicable to the separation of H and CH₄, even when there is only a small quantity of H; in this latter case, however, it may be used, but it is necessary to measure the volume of CO₂ formed. It must be observed that with time the palladium-coated asbestos loses its catalytic properties. The best method of absorbing the hydrogen in the mixture is to use palladium sponge, as Hempel advised, but it is unnecessary to heat to 120°, a temperature of 70° is quite sufficient.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 710.

Preparation of Zirconia.—E. Wedekind.—The method adopted by the author is as follows:—An intimate mixture of 20 parts of zircon, 12 parts of lime, and 7 parts of carbon is heated in a carbon crucible in the electric furnace. The crucibles, which are only three-quarters full and uncovered, are heated by means of a current of 1000 amperes and 50 volts for seven minutes. After the reaction the graphite cover is put on to prevent oxidation. After cooling, wash with cold water, then with hydrochloric acid. The carbide is then dissolved in aqua regia; filter through asbestos, and evaporate to dryness. The iron is removed from the residue, either by precipitating the ZrO₂ and FeS by means of sulphide of ammonium, and then dissolving the sulphide of iron with sulphurous acid, or by precipitating the sulphide of iron with sulphide of ammonium in the presence of tartaric acid. When treated with a current of chlorine, carbide of zirconium gives the anhydrous chloride, ZrCl₄, which dissolves in water, forming the oxychloride. This oxychloride can be obtained in a well crystallised form by dissolving the chloride in hydrochloric acid. When heated to 100–110° it becomes less soluble in water.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 81.

Anodic Decomposition of Solutions of Cobalt and of Nickel.—Alfred Cohen and Moritz Gloser.—A. Cohen has shown the difference of susceptibility with which nickel and cobalt appear to form higher oxides (*Zeit. Phys. Chem.*, vol. xxv., p. 651). In collaboration with M. Gloser, he has examined the anodic decomposition of solutions of nickel and cobalt. In slightly alkaline solutions, the sulphates of these metals give oxides at voltages of 1.20 for cobalt and 1.30 for nickel. In slightly acid solutions nickel does not form an oxide, and cobalt requires 1.52 volts. In strongly acid solutions no oxide is formed either of nickel or cobalt. Precipitated oxide of cobalt dried at 40° has a composition which varies from Co₂O₃·3H₂O and Co₂O₃·2H₂O. Cobalt and nickel can be separated electrolytically. The conductivity of the solutions must be increased by the addition of sulphate of potassium. A platinum cathode is used, and bichromate of potassium as a depolarising agent. The electrolysis is carried out in hot solution with a current of 2.3 to 2.4 volts, and 0.10 to 0.15 ampère, and the separation is complete. This method is very useful for the detection of cobalt in the presence of nickel; cobalt, even in small quantities, gives a dark deposit on the platinum anode in neutral solution.—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 9.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough. Society of Chemical Industry, 8. "Cyanide Manufacture," by Dr. J. Grossmann.

TUESDAY, 8th.—Faraday Society, 8. "Total and Free Energy of the Accumulator," (adjourned Discussion), by R. A. Lehfeldt, D.Sc. "Bitumen in Insulating Compositions" (Part I.), by D. A. Sutherland, F.I.C., F.C.S. "Notes on Aluminium Welding," by Sherard Cowper-Coles. "Electro-chemical Installation at the Borough Polytechnic Institute," by F. M. Fiskin, Ph.D.

WEDNESDAY, 9th.—Society of Arts, 8. "Furnaces Suitable for Jewellers' Work, Enamelling, Art Casting, and other similar Industries," by Henry Hardinge Cunyngame, C.B.

THURSDAY, 10th.—Society of Arts, 4.30. "India's Place in an Imperial Federation," by J. M. Maclean.

FRIDAY, 11th.—Physical, 8. (At the Royal College of Science, South Kensington). "A Method of Mechanically Reinforcing Sounds," by Rev. T. C. Porter. "The Simmance-Abady 'Flicker' Photometer," by Messrs. Simmance and Abady. Exhibition of a Conduco-meter, by R. Appleyard. A Model to Illustrate various Properties of Wave-motion, by Prof. L. R. Wilberforce.

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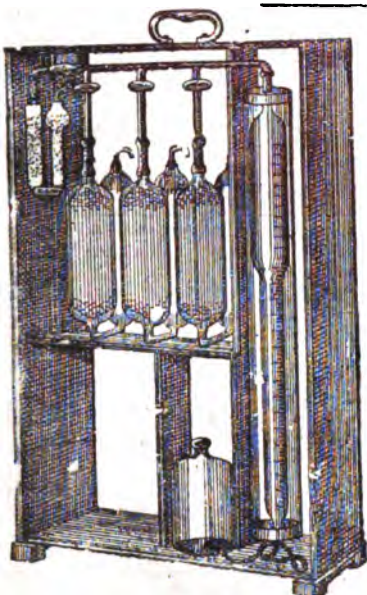
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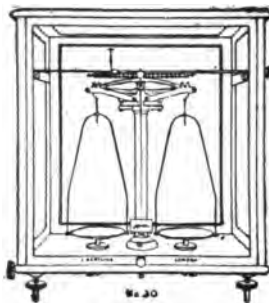
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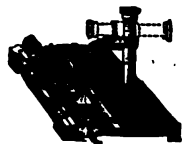


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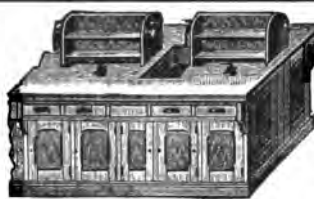
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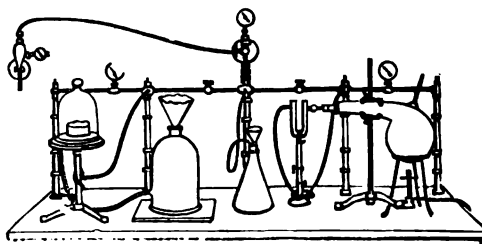
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2298.

THE SLOW COMBUSTION OF METHANE AND ETHANE.*

By WILLIAM A. BONE.

I MAY perhaps be allowed to explain my reasons for reopening what I am well aware is one of the most controverted questions in the whole domain of chemistry. Let me say at once that I have no new general theory of hydrocarbon combustion to bring forward; but during the past three or four years I have, in conjunction with two of the research students at Owens College (Messrs. R. V. Wheeler and W. E. Stockings), been engaged upon an investigation on the slow combustion of methane and ethane at temperatures below their ignition-points, the results of which throw some new light on the question at issue. It is my intention to extend the work to other typical hydrocarbons in the hope that the gradual accumulation of experimental facts may at some future time provide a sure basis for a general theory of hydrocarbon combustion. Meanwhile it seemed to me that the meetings of this Chemical Section afforded a fitting opportunity of communicating and discussing these new observations, of obtaining suggestions for future work, and possibly, also, of arranging some form of co-operation among those workers who are specially interested in this field of inquiry.

It seems to me unnecessary to make more than a passing reference to the theories which up to the present have been advanced to explain the mechanism of hydrocarbon combustion. I must, however, say a word with regard to two of them which involve the idea of the "*preferential*" combustion, either of hydrogen or of carbon. The older idea, that in a defective oxygen supply the hydrogen of a hydrocarbon burns preferentially to the carbon, is unsupported by experimental evidence, and I suppose now hardly finds acceptance among chemists at any rate. On the other hand, the opposite view, that the carbon burns preferentially to the hydrogen, was put forward, originally by Kersten in 1861 I believe, to explain the well-known fact that when such a hydrocarbon as ethylene is exploded with just sufficient oxygen to burn the carbon to carbon monoxide, the cooled products consist of carbon monoxide and free hydrogen—



Professor Smithells in 1892 was led to indorse this view as the result of his analyses of the interconal gases of hydrocarbon flames.

It seems to me that the idea of "*preferential combustion*," whether of hydrogen or of carbon, is closely allied to the old doctrine of "*elective affinity*," and that it is hardly to be reconciled with modern conceptions of the nature and conditions of chemical change in a homogeneous system. Furthermore, it may be pointed out that the evidence usually adduced in support of the contention that carbon burns preferentially to hydrogen is wholly derived from experiments on the oxidation of hydrocarbons at very high temperatures, either in the flame, or in the explosion wave. Under these conditions it is practically impossible, by any means at our command at present, to distinguish the character of the *primary* oxidation in the case of a hydrocarbon, for since the velocities of all the reactions concerned are enormously great, the final state of equilibrium is almost instantaneously established.

The experiments on the slow combustion of methane and ethane, which have led me to make this communication, have been carried out at temperatures far below the ignition-points of the gases—that is to say, at temperatures where the oxidation velocities are sufficiently small to allow of their being easily measured. It is also important to observe that either of the hydrocarbons in question interacts with oxygen at temperatures below those at which the velocities of any of the undermentioned possible secondary changes become appreciable:—

- i. $2H_2 + O_2 = 2H_2O.$
- ii. $2CO + O_2 = 2CO_2.$
(moist)
- iii. $CO + H_2O \rightleftharpoons CO_2 + H_2.$
- iv. Reduction of CO_2 , or of H_2O , by carbon.

Therefore, by suitably choosing our temperature conditions we have been able to exclude the possibility of these reactions occurring, and so to prevent the complete masking of the *primary* reaction by secondary changes.

The details of these experiments either have been, or shortly will be, published elsewhere (*Trans. Chem. Soc.*, 1902, lxxxii., 535; 1903, lxxxiii.), and we need therefore only here indicate the general character of the results.

In the first place, we should say that the mixtures of methane (or ethane) and oxygen employed usually contained just sufficient oxygen to burn the carbon of the hydrocarbon to carbon monoxide (*e.g.*, mixtures of two volumes methane with one volume oxygen, or of equal volumes of ethane and oxygen).

The lowest temperature at which such mixtures of methane and oxygen interact, when sealed up in a borosilicate glass bulb at atmospheric pressure, and afterwards placed in a constant temperature air-bath, is somewhere about 300°; in the case of the mixtures of ethane and oxygen it is about 225°. At all temperatures ethane is oxidised much more rapidly than is methane, other conditions being equal.

Under such conditions a portion of the hydrocarbon is burnt to, finally, carbon dioxide, carbon monoxide, and steam, *without any liberation of free hydrogen or separation of carbon*, while a portion of the original hydrocarbon always remains intact.

Below are tabulated the analyses of the products from two typical experiments:—

Products from Mixture	Products from Mixture
$CH_4 = 66.9, O_2 = 33.1,$ maintained Seven Days at 350°.	$C_2H_6 = 49.8, O_2 = 50.2,$ maintained Fifteen Hours at 250°.
$CO_2 \dots \dots \dots 14.0$	$CO_2 \dots \dots \dots 15.9$
$CO \dots \dots \dots 16.3$	$CO \dots \dots \dots 41.2$
$O_2 \dots \dots \dots 0.9$	$O_2 \dots \dots \dots \text{nil}$
$CH_4 \dots \dots \dots 68.8$	$C_2H_6 \dots \dots \dots 42.9$
Per cent contraction in volume on open- ing cooled bulb under mercury (nearly) $\dots \dots \dots 32.0$	34.76

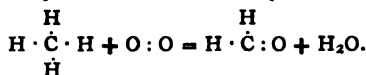
We next devised an apparatus in which the reacting gaseous mixtures can be continuously circulated day and night, at a practically uniform rate, (1) over a surface maintained at a constant temperature; and (2) through suitable washing and cooling arrangements for the removal of soluble or condensable intermediate products. A manometric arrangement enables us to take pressure records of the gas in the apparatus at regular time-intervals throughout a given experiment, which may often extend over many consecutive days and nights. The records so obtained show, in the case of both methane and ethane, a regular and continuous fall of pressure throughout the oxidation.

The experiments with methane reveal the fact that formaldehyde plays an important rôle as an intermediate

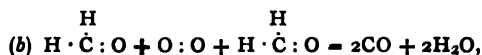
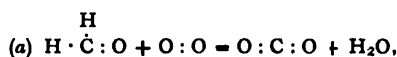
* A Paper read before the British Association (Section B), Southport Meeting, 1903.

product; that, indeed, the oxidation involves at least two distinct stages, namely:—

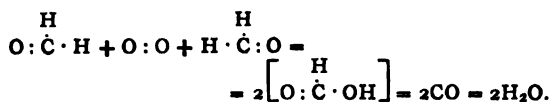
1. A primary oxidation to formaldehyde and steam—



2. The subsequent further rapid oxidation of the formaldehyde to carbon monoxide, carbon dioxide, and steam. This may best be considered as the result of two simultaneous reactions, namely:—



possibly the latter may involve the formation and very rapid decomposition of formic acid. Thus—

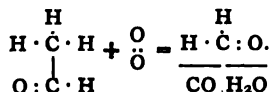


In the case of ethane we are able to distinguish the successive formations of (1) acetaldehyde, and (2) formaldehyde, as intermediate products. The experimental results are consistent with the following view of the case, namely:—

1. That the primary oxidation involves the formation of acetaldehyde and steam—



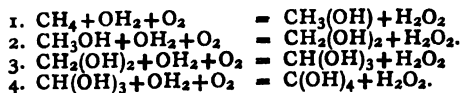
2. That the acetaldehyde is further rapidly oxidised to carbon monoxide steam and formaldehyde—



3. That the formaldehyde suffers further oxidation as indicated above.

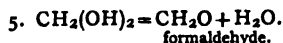
These views, it may be stated, are supported by experiments on the oxidation of acetaldehyde.

I wish it to be understood that I have provisionally adopted the explanations just given of the oxidation stages of methane and ethane as a convenient working hypothesis because they express most simply the observed facts. Professor Armstrong has recently given us (*Trans. Chem. Soc.*, lxxxiii., 1088) a very suggestive general theory of combustion which embodies his dictum that chemical interchange and electrolysis must be regarded as interchangeable equivalent terms. Applied to hydrocarbons (e.g., methane) the theory involves the successive "hydroxylation" of each hydrogen by an indirect process, the oxygen being transferred electrolytically across "conducting" water, as indicated by the following scheme:—

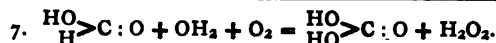
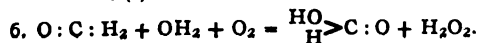


The hydrogen peroxide formed being in part decomposed by heat, and in part acting as depolariser.

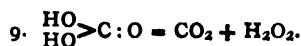
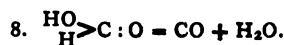
The hydroxylated molecules thus produced may decompose, as for instance:—



and then the formaldehyde is further indirectly oxidised to (1) formic acid, (2) carbonic acid, thus:—

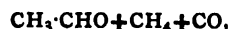


The formic and carbonic acids thus produced then decompose as follows:—



It does not come within the province of this paper to discuss this electrolytic theory of chemical change; it should, however, be pointed out that Professor Armstrong's views demand the formation of an alcohol in the *primary* oxidation of a saturated hydrocarbon. Although I have never failed to obtain a marked formation of aldehydes in my experiments on methane and ethane, I have so far searched in vain for alcohols; if the latter are produced during the primary oxidation, they are very rapidly further oxidised to the corresponding aldehydes which must be presumed to be more stable under these conditions.

The question now arises whether these reactions which undoubtedly occur at low temperatures also occur at the higher temperatures of hydrocarbon flames. My own view is this:—The velocities of these "low temperature" reactions will rapidly increase as the temperature rises, and so long as aldehydes can exist, aldehyde formation will occur. But aldehydes themselves decompose at high temperatures; thus acetaldehyde is known to yield carbon monoxide and methane—



and similarly formaldehyde yields carbon monoxide and hydrogen—



and possibly within certain temperature limits these reactions are reversible.

The production of formaldehyde in the oxidation of methane, for example, will only be limited by the temperature at which formaldehyde is incapable of existence, whatever that may be.

We shall have to take into account similar considerations in discussing other probable changes, as, for example, (1) the further oxidation of aldehydes, and (2) the purely thermal decomposition of hydrocarbons. All these possible reactions call for further careful investigation. As yet we have so few well-established data that it seems premature to formulate general theories. The subject is very complex, and is beset with many and great experimental difficulties, but it is surely within our power to overcome them, especially if a sufficient number of workers will co-operate.

Dr. T. L. Phipson's recent work, "Researches on the Past and Present History of the Earth's Atmosphere," has just been translated into Japanese by Prof. Sakatibara, Lecturer on Pharmacy at the Kato Hospital, Tokio.

F. E. Becker and Co. (W. and J. George, Ltd., Successors).—The new Catalogue of Chemical Apparatus recently issued by this enterprising firm is undoubtedly the most complete and exhaustive one of its kind that we remember having come across. Practically every item is accompanied by an illustration immediately adjoining it, and the great majority of the woodcuts used have been specially engraved for this list. The catalogue contains a complete list of chemicals, reagents, and standard solutions; it covers all new and improved forms of apparatus for general laboratory use, and is provided with an excellent index, each piece of apparatus being indexed under the several headings where it would be sought for. Messrs. George, Ltd., will forward the catalogue gratis to workers and teachers in science who apply for it.

ON ACRIDINES.*

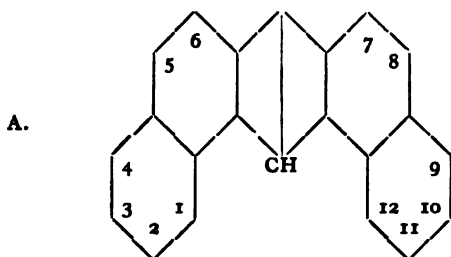
By ALFRED SENIER, Ph.D.,
Professor of Chemistry in Queen's College, Galway.

(Continued from p. 269).

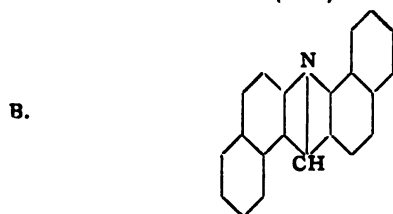
V. Naphthacridines.

THE naphthacridines are obtained by methods analogous, generally, to those for the preparation of acridines. They are stable crystalline compounds with the physiological action and the characteristic fluorescence of their simpler analogues. Like the latter, they form dihydrides, salts, alkalides, and, as Mr. Goodwin and I find, they also form dihalides.

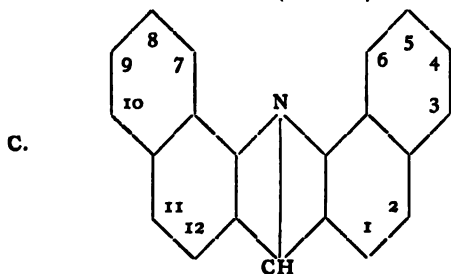
1. Possible Isomeric Types:—



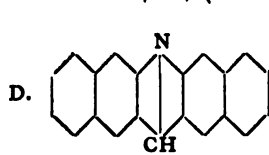
$\beta N \beta$
 $\alpha C \alpha$ (Reed).



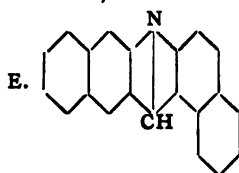
$\beta N \alpha$
 $\alpha C \beta$ (Ullmann).



$\alpha N \alpha$
 $\beta C \beta$ (Senier and Goodwin).

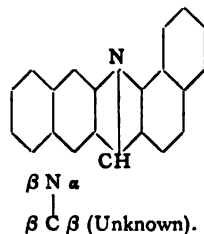


$\beta N \beta$
 $\beta C \beta$ (Unknown).



$\beta N \beta$
 $\beta C \alpha$ (Strohbach).

F.

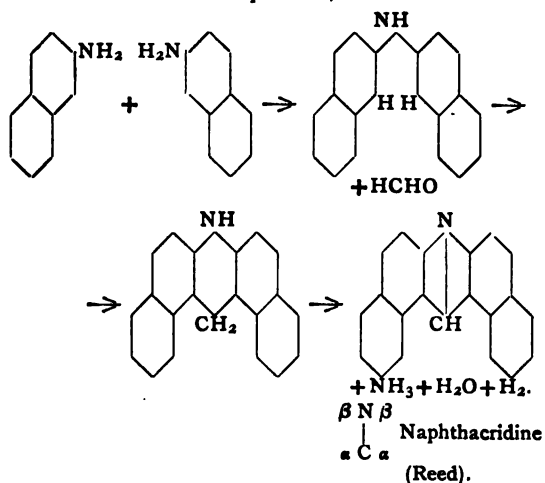


The notation is, I think, more convenient than that used by Ullmann (*Ber.*, 1903, xxxvi., 1037) after Graebe, or by Möhlau and Haase after Strohbach (*Ber.*, 1901, xxxiv., 4147). The numbering is taken from Möhlau and Haase (*Ber.*, 1902, xxxv., 4173).

2. Formation and Constitution:—

i. *Diamine and Aldehyde Method.*—The first naphthacridine, *ms*-phenylnaphthacridine, was obtained by Claus and Richter (*Ber.*, 1884, xvii., 1590) by condensing benzoyldi- β -naphthylamine by means of a dehydrating agent. This may be regarded as a modified aldehyde diamine method. The first simple naphthacridine was prepared by Reed (*Journ. Prakt. Chem.*, 1886, [2], xxxiv., 160; 1887, xxxv., 298), who condensed two molecules of β -naphthylamine with formaldehyde (methylal and hydrochloric acid). That this naphthacridine is $\beta N \beta$ has

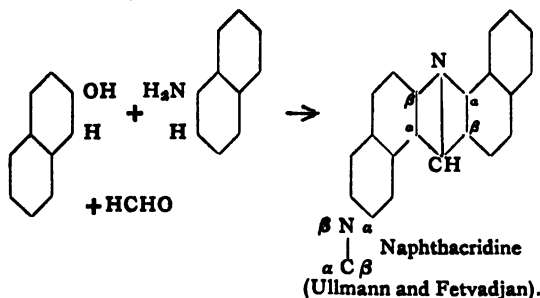
been generally accepted after the evidence adduced by Strohbach (*Ber.*, 1901, xxxiv., 4148) as to the greater readiness with which the α -position substitutes. Di- β -naphthylamine and naphthacridine dihydride are formed doubtless as intermediate products, thus:—



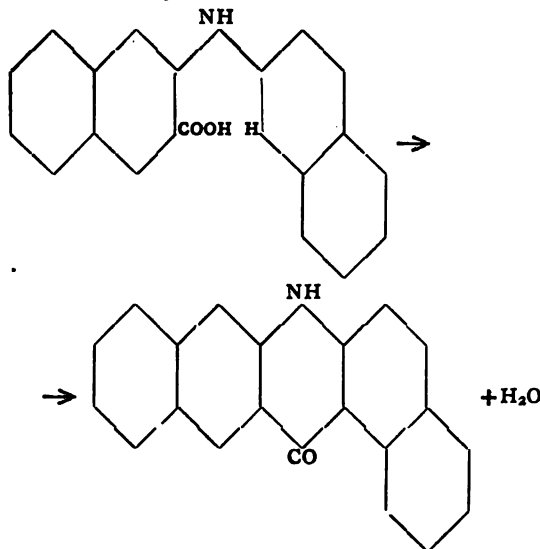
This reaction is the subject of two important papers by Morgan (*Journ. Chem. Soc.*, 1898, lxxxiii., 536; 1900, lxxvii., 814), who describes another very curious compound obtained in the same reaction, "isonaphthacridine." Möhlau and Haase (*Ber.*, 1902, xxxv., 4164) in a recent paper have re-investigated this compound, and its constitution is still a problem of great interest. Modifications of Reed's method have been employed by Möhlau and Haase (*Ber.*, 1902, xxxv., 4172; 1903, xxxvi., 591), and recently Ullmann and Fetvadjan (*Ber.*, 1903, xxxvi., 1027) from β -naphthol, α -naphthylamine, and

* Abstract of a Paper read before the British Association (Section B), Southport Meeting, 1903.

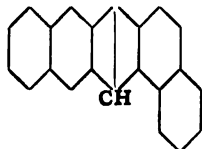
formaldehyde, have discovered a new naphth-acridine, the β N α isomeride (Formula B.), thus:—



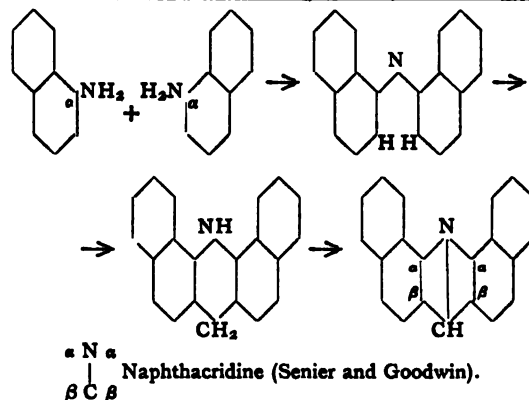
- ii. *Diamine and Acid Method.*—Ris (*Ber.*, 1883, xvii., 2029), in applying this method to naphthacridines, prepared the phenylnaphthacridine of Claus and Richter from di- β -naphthylamine and benzoic acid. Möhlau obtained the acridone of a new type from di- β -naphthylamine-2:3-mono-carboxylic acid, thus:—



Strobbach by reducing this acridone prepared the corresponding acridine (Formula E.):—



- iii. *Methylene Di-iodide and Diamine Method.*—By this method Mr. Goodwin and I (*Journ. Chem. Soc.*, 1902, lxxxi., 280) obtained Reed's naphthacridine working with β -naphthylamine, while in the corresponding experiment with α -naphthylamine we succeeded in isolating a new type α N β naphthacridine, thus:—



Two nitro-derivatives of this base were obtained and a disulphonic acid recently described by Möhlau and Haase (*Ber.*, 1902, xxxv., 4173) belongs to the same type.

I have just succeeded in obtaining the β N α base of Ullmann and Fetvadjan by the methylene di-iodide method.

(To be continued).

ESTIMATION OF MORPHINE IN OPIUM.

By P. L. ASLANOGLU.

THIS no doubt will add one more process for the estimation of morphine in opium to the many already existing, but it must not be assumed that the past researches of my *confrères* have been disregarded by me; on the contrary, having worked with their methods I failed to obtain satisfactory results, perhaps owing to their not being clearly explained. I have, however, tried to the best of my knowledge, after having experimented a great deal, to work out an easy and quick method for the estimation of morphine in opium.

Take 10 grms. or so of a fair sample of opium which has been taken from the bulk and well mixed in a machine, and rub it down well in a small glass mortar with a small quantity of distilled water, and when this has extracted what it can from the opium put it into a beaker, and again add water to the mortar, rubbing it down until all the 10 grms. of opium has been well mixed with water, using only 150 c.c. of water for that manipulation. This should be left to stand for twelve hours in soak, and then decant the brownish red liquid on to a filter, using double filters, leaving the opium behind. Add to it another 150 c.c. of water, and let it stand in soak for an hour or so, stirring from time to time. The first filtrate containing the alkaloids of opium is evaporated to dryness on a water-bath. The second portion of the 150 c.c. aqueous extract of opium is filtered as before, and the filtrate evaporated to dryness in the same evaporating basin which has been used for the first evaporation; the remaining opium is for a third time treated with 200 c.c. of water filtered as before, and evaporated. This dry aqueous extract represents the 10 grms. of opium taken. It is then dissolved in 75 c.c. of water, and filtered, using double filters; the basin and filter-paper are well washed with 25 c.c. more of water till the whole measures 100 c.c. To this 100 c.c. filtrate containing the alkaloids of the opium, 25—30 c.c. of 94 per cent alcohol are added, and well stirred for half-an-hour. After this 3—4 c.c. of 10 per cent solution of ammonia (sp. gr. 0.959) are added, and well stirred for half-an-hour,

and left for twelve hours to precipitate; it is best not to leave it more than twelve hours.

3.5—4 c.c. of 10 per cent solution of ammonia is to be added for 10 grms. opium for analysis containing 9—11 per cent morphine, but if the opium contains between 11—13 per cent morphine the ammonia ought to be increased to between 4—5 c.c.; however, experience will show this to the analyst. In fact the correct way will be to take a very small portion of the filtered aqueous extract, dilute it with water, and titrate it with $N/10$ NH_3 , using as indicator phenolphthalein. Once we know the percentage of acidity of the solution, we can estimate accordingly the amount of NH_3 required for the whole solution in order to precipitate the morphine.

After the twelve hours have elapsed, pour the liquid through a tared filter-paper, leaving the precipitated morphine behind in the flask (flasks should be used with good indiarubber corks or glass-stoppers for precipitating the morphine, and not open beakers). Then 25 c.c. of water is added to it to wash it, and the washings with the morphine are transferred to the tared filter-paper, and washed well with another 25 c.c. of water; let it drain well, and partly dry in the oven at $60^\circ C$. When this is done, the filter with the morphine is well washed with pure ether; let it drain again, and put it in an oven, and dry at first at $60^\circ C$., and after an hour increase the temperature to $75^\circ C$. until well dry, which takes between three to four hours. Transfer the filter with the morphine into a desiccator, let it cool well, and weigh quickly.

It must not be thought that when we obtain the amount of morphine as above from 10 grms. of opium that is the real and true amount of morphine contained in the opium. Here is the point where, perhaps, some of my *confrères* fall into error and give low results in the percentages of morphine in the opium, and no doubt why in most chemical books, in speaking about the Smyrna opium, say that it does not contain more than 10 per cent of morphine when dried and analysed, which brings it down to 8.065 per cent of morphine when fresh, taking into consideration that Smyrna opium contains on an average 24 per cent of water when fresh. Such low percentages are absurd with good qualities of Smyrna opium.

For an example, let me bring here the method used by the British Pharmacopœia (1893) given in the test for opium (pp. 295—297) the following:—"The crystals should weigh 10 grains, or not less than $9\frac{1}{2}$ and not more than $10\frac{1}{2}$ grains, corresponding to about 10 per cent of morphine in the dry powdered opium."

And again, the British Pharmacopœia takes 140 grains of dried opium and make their own solutions, and then keep a certain amount of solution, which corresponds to 100 grains of opium, but it seems a rather round-about way; why not take all the amount of opium and exhaust it well? Are they sure that that amount of solution taken represents the 100 grains of opium and not less or more of it?

When the morphine has been weighed and the tare of the filter-paper subtracted, the following calculation must be made in order to find the true amount of morphine, viz., from the time the ammonia has been added to the time of the last washing with water, the number of hours must be counted and the temperature of the day also taken into account. For the following calculation let us take $15^\circ C$. as an example, but as the temperature of the day varies with the season, say, 20 — 25 — $30^\circ C$., the solubility of the morphine is in direct ratio to the temperature; so as many hours as have elapsed the number of hours should be multiplied by the factor 0.004583, which is the morphine dissolved in 100 c.c. of the liquid in one hour's time (if the quantity of the liquid increases so much more per cent of morphine will be dissolved); then the percentages are worked out, and the true amount of morphine is obtained. Because to the watery extract we added alcohol, ammonia, and the water present for the extraction, the morphine which is precipitated on standing for twelve hours is redissolved in small quantities, as found by my experiments.

This with the amount of water for washings brings it to the factor 0.004583 per 100 c.c. of liquid in one hour's time. For higher temperatures the factor will be as follows:—

$20^\circ C$.		0.004910
$25^\circ C$.		0.005237
$30^\circ C$.		0.005564

and so on.

Therefore taking the watery extract to be 100 c.c. with 30 c.c. alcohol and 3—4 c.c. ammonia, then 50 c.c. water for washings, this would make altogether 184 c.c. of liquid and twelve hours standing at $15^\circ C$.

$$\frac{184 \times 0.004583 \times 12}{100} = 0.10119264,$$

which is the amount of morphine required to be added to the found morphine by weight in the 10 grms. of opium.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, November 18th, 1903.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Allan Baguley, B.Sc., University College, Bangor; James Rocheid Forrest, D.P.H., Kirkee, near Poona, India; Harry James Glover, 33, Albert Road, Stroud Green, N.; John Augustus Goodson, 19, Darnley Road, Hackney, N.E.; Alfred Henry Hoyt, 4, Montgomerie Road, Southsea; Bernard Middleditch, B.A., Woodcroft, Harrow-on-the-Hill; Bertram Prentice, Ph.D., D.Sc., Royal Technical Institute, Salford; Frederick Henry Streatfeild, 9, Crescent Road, South Tottenham, N.; William Wood Underhill, 10, Hartham Road, Holloway, N.; Francis Langston Watt, 111, Lauderdale Mansions, Maida Vale, W.

Of the following papers those marked * were read:—

*149. "The Union of Carbon Monoxide and Oxygen and the Drying of Gases by Cooling." By A. F. GILVAN.

The following experiments were made in order to investigate whether the drying of an explosive mixture of carbon monoxide and oxygen by exposure to low temperatures was sufficient to prevent chemical union taking place when the gas was sparked after it had regained the ordinary temperature.

A small glass gas-holder containing the explosive mixture was sealed to the following apparatus arranged in series:—

(1) A small bubbler containing water, (2) a stopcock, (3) a vertical glass spiral, (4) a glass tube, 1 c.m. in diameter, furnished with platinum terminals with a spark gap of about 4 m.m., (5) a stopcock, (6) a Töpler pump. Stopcocks were sealed as side-tubes between (2) and (3), and between (5) and (6). The carbon monoxide was prepared by the interaction of "pure" sulphuric and formic acids, the oxygen being obtained by heating potassium permanganate; the gases were collected and stored over water, and the proportion was correct to within 1 per cent.

A slow current of air was aspirated through the apparatus by means of the side-taps, while the whole apparatus between them was thoroughly heated. The spiral was then surrounded by a freezing mixture, and the tube between it and the pump was heated to the softening point of the glass. After some time, the current of air was stopped and the heating discontinued. The apparatus was then completely exhausted as far as the bubbler by means of the Töpler pump, and the explosive mixture slowly admitted at the rate of one bubble per second. When the gas in the apparatus was under atmospheric pressure, the tap of the gas-holder was closed, and sparks from an induction coil

were passed through the explosion tube which the gas was now at the temperature of the atmosphere.

In the first experiments, where liquid air was used, care had to be taken that this cooling agent was not too fresh, as it was then sufficiently cold to liquefy the explosive mixture. No explosion took place on passing sparks from an induction coil which, at the same time, was giving 12 m.m. sparks in the air, although the sparks in the gaseous mixture were usually surrounded with a little ball of blue flame. When the glass spiral was allowed to regain the ordinary temperature, the moisture which had been condensed in the spiral slowly diffused into the explosion-tube, and a single spark exploded the mixture with a sharp report.

On sparking the mixed gases which had been cooled in a mixture of solid carbon dioxide and alcohol (-80°), there was no explosion, and the little ball of flame round the sparks had much the same appearance as when the gases had been dried at -180° , but when the glass spiral had acquired the ordinary temperature, a single spark produced a sharp explosion. When the gaseous mixture had been cooled to -15° and allowed to regain the ordinary temperature, the first spark always caused an explosion, but this did not occur after cooling below -50° . When dried between -50° and -35° , faint sparks did not, as a rule, cause the mixture to explode, although powerful sparks always produced this effect. The freezing mixture employed was either liquid air or solid carbon dioxide in alcohol, and when kept in a vacuum-vessel its temperature arose only about half a degree per minute, even when a current of air was passing through the spiral.

A single powerful spark, when passed through the mixture (after drying between -50° and -35°), frequently produced no effect, whereas an explosion always occurred on passing the second or third spark.

The explosion produced by powerful sparks in the gases dried between -50° and -35° is of a very different character from that obtained with the wet gases; the latter is very quick and violent, and gives a metallic click, but the former takes place quietly, and the explosive wave often travels quite slowly along the tube (compare Dixon, *Phil. Trans.*, 1884, clxxv., II., 630). The wave proceeding from these feeble explosions always stopped directly it reached the cold part of the spiral, and the gas in this part of the apparatus was found to be unaltered, but when the gas was moist and the spiral at the ordinary temperature, the explosion passed to the furthest part of the apparatus.

The platinum terminals were now replaced by (1) a silver wire, (2) a gold wire; each of these was heated to redness and then fused by an electric current, without causing any visible union in the explosive mixture, which had been dried at about -80° . In order to find out whether platinum would act catalytically on the dried or partly dried gases (compare Dixon, *loc. cit.*) a tube, in which the platinum terminals were replaced by a coil of platinum wire, was sealed in place of the sparking-tube, and the apparatus dried as before. The explosive mixture was then allowed to enter through the spiral, which was kept at various temperatures.

With a mixture dried at about -35° , the platinum acted catalytically, and in becoming heated to redness brought about a quiet and feeble explosion. When, however, the mixture was dried at temperatures between -80° and -180° , the platinum still acted catalytically and glowed for several seconds, but there was no other sign of chemical action. After the glowing had ceased, the coil was kept at a white heat for several minutes by means of an electric current, and the gas was then pumped off and collected. About one-eighth of the gaseous mixture was absorbed in caustic potash solution and the residue was still explosive, showing that combination was far from complete.

At Sir William Ramsay's suggestion, the author calculated the amount of moisture present in the mixture after cooling (compare *Trans.*, 1886, xlix., 46), the following data being employed:—

Temperatures ..	-61°	$-56^{\circ}5'$	-51°	-45°	-36°
Pressures in m.m.	0.008	0.01	0.029	0.052	0.160

When the vapour pressure of the water is less than about 0.03 m.m., as is the case with the mixture after cooling at -50° , the gases will not explode. When the vapour pressure is less than about 0.16 m.m., the explosion is very feeble.

In the first case, the amount of water vapour present is about one part in twenty-four thousand by volume, and in the second, one part in five thousand. At -61° , the amount of water vapour would be about one part in a hundred thousand of gas.

It would appear then that the mixture will not explode when sparked at the ordinary temperature if there is less than one mol. of water vapour to twenty-four thousand mols. of the gas.

These figures must, however, be taken as being only approximate, since below -50° the vapour pressure of ice falls to half its value for a decrease of about 7° , and, moreover, it is not known whether the glass of the apparatus exerts any drying effect on the contained gas.

DISCUSSION.

Sir W. RAMSAY pointed out the interest of Mr. Girvan's experiments in connection with surface-layers on glass. The water vapour in contact with the water-layer on the glass must have a vapour-pressure comparable with, or less than the vapour-pressure in contact with ice at -185° . This film is removed on heating the glass in a current of dry air, and is not removed when the mixed gases, dried at -60° , are allowed to enter the dried tube. Such questions are of very great interest from the standpoint of molecular physics, and Mr. Girvan, he knew, hoped to attack these and similar problems at an early opportunity.

Dr. SCOTT suggested that the water which adhered to the glass might be there not as a gaseous layer but either as a hydrated silicate or in combination with alkali.

*150. "Simplification of Zeisel's Method of Methoxyl and Ethoxyl Determinations." By W. H. PERKIN.

In this process, a long-necked distilling flask was employed without any condensing arrangement, the tube for the current of carbon dioxide being passed down the neck to within a short distance of the hydriodic acid. It was eventually found that as long as the temperature of the glycerin bath was so adjusted that actual distillation of the acid into the delivery tube did not take place, no appreciable quantity of hydrogen iodide passed forward into the silver nitrate flasks. The acid used boiled at 126° and had a sp. gr. of 1.68 approximately.

The following arrangement has been found to prevent the silver nitrate solution from being sucked back into the distilling flask after a sudden ebullition of hydriodic acid. Two small flasks are used as usual, but the tube conducting the carbon dioxide and methyl iodide vapour, instead of passing into the silver solution, is kept some distance above its surface. The flasks are then connected with a syphon tube, one arm of which reaches to within a short distance of the solution in the first flask, whilst the other arm dips a little below the surface in the second. By this arrangement, the methyl iodide is chiefly absorbed by the surface of the silver solution, but any escaping is caught as it bubbles through the second quantity; then, if any such drawing back takes place, some of the solution passes into the first flask, and as soon as the pressure increases is forced back again into the second.

This method of determining the methoxyl group gave very good numbers, and can be used equally well for determining the ethoxyl group, but in this case the numbers are not usually so accurate, being generally a little less than the calculated quantity.

*151. "The Rusting of Iron." Part II. By G. T. MOODY.

The author has further investigated the causes of the rusting of iron, more particularly with reference to the influence of soluble substances, and finds that the salts of strong acids, such as sodium chloride and sulphate, potassium sulphate, ammonium sulphate, magnesium chloride and sulphate, calcium chloride and sulphate, and potassium chlorate have no retarding influence on rusting. These

salts do not combine with, and are not decomposed by, carbonic acid. Compounds which inhibit rusting may be divided into two classes. The first contains substances having an alkaline reaction, such as sodium carbonate, hydroxide, phosphate, and borate, ammonium carbonate, and barium and calcium hydroxides, all of which directly absorb and combine with carbonic acid. The second class includes salts of weak acids, such as potassium and sodium nitrites, sodium formate, sodium acetate, potassium ferrocyanide and chromate. These salts are all decomposed by carbonic acid. Sodium nitrite solution, for example, after exposure to air becomes alkaline, and contains sodium carbonate. A solution of 10 grms. of the nitrite, through which a slow stream of carbon dioxide was passed for nine days, contained 1.585 grms. of sodium carbonate. Similarly, potassium ferrocyanide solution, when exposed to air, slowly evolves hydrogen cyanide and becomes alkaline. This change occurs more rapidly when carbon dioxide is passed through the solution, the escaping gas having the odour of hydrogen cyanide and precipitating silver cyanide from a solution of silver nitrate. Potassium ferricyanide is a salt of a weak acid which exceptionally does not appear to retard rusting. This substance is, however, reduced by iron whether its solution be exposed to air or not, the metal becoming covered in either case with a mass of insoluble, greenish-blue cyanide.

It may therefore be concluded that the influence of any particular compound on the atmospheric rusting of iron depends on its behaviour towards carbonic acid, and that only those substances which combine with or are decomposed by carbonic acid inhibit rusting.

Dunstan has stated (*Proceedings of the Royal Artillery Institution*, 1899, v., 26, and *Proc.*, xix., 150) that the metals which rust in air are oxidised by hydrogen peroxide, whilst those which are not oxidised by this reagent do not rust in air. Iron, zinc, and lead are cited as examples of the first class, and copper, silver, and nickel as types of the second. It is noteworthy that iron and zinc rapidly decompose aqueous carbonic acid, whilst copper, silver, and nickel are indifferent to the acid. Having regard to this, and also to the fact that Georgis (*Gazetta*, 1891, xxi., 510) has shown that hydrogen peroxide, when carefully freed from carbon dioxide, is practically without action on magnesium, it appeared probable that iron would not be oxidised by pure hydrogen peroxide. The author has investigated this question by leaving a specimen of distilled hydrogen peroxide in contact with iron for fourteen days. No oxidation of the iron was observed, but on adding to a further portion of the pure peroxide containing iron a drop of hydrochloric acid or a solution of carbon dioxide, hydrated ferric oxide was formed.

In the light of the experiments described, the aerial rusting of iron cannot be attributed to hydrogen peroxide, but must be regarded as a change involving the interaction of iron and acid, and subsequent formation of rust by the oxidation of ferrous salt.

DISCUSSION.

Dr. RIDEAL remarked that Müntz had shown (*Comptes Rendus*, 1891, cxii., 1142) that calcium nitrite in sterilised soil gave off nitrous acid rapidly in presence of carbonic acid, and that he had noticed this reaction in bacterial sewage filters.

Mr. W. A. DAVIS pointed out that the decomposition brought about in aqueous solutions of sodium nitrite and potassium ferrocyanide, although at first sight surprising, was a necessary consequence of the principle of mass action. As both nitrous and hydrocyanic acids are volatile, the conversion of their salts into carbonates by an excess of carbonic acid should be complete after a sufficient interval of time.

Dr. MOODY, in reply, said that the sodium nitrite used, which was a well-crystallised specimen, having a high degree of purity and quite free from carbonate, was so sensitive to carbon dioxide that the gas, after passing through the solution, immediately reacted with potassium iodide and starch solution.

152. "Constitution of Ethyl Cyanoacetate. Condensation of Ethyl Cyanoacetate with its Sodium Derivative." By F. G. P. REMFRY and J. F. THORPE.

When ethyl sodiocyanoacetate is heated in alcoholic solution for two hours at 100° with a molecular proportion of ethyl cyanoacetate, a 70 per cent yield of the compound, $\text{CN}\cdot\text{CH}_2\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, is produced, which crystallises from dilute alcohol in long needles, melts at 53°, and distils with partial decomposition at 235° under 20 m.m. pressure. On boiling with sodium carbonate solution, this substance dissolves, and, on acidifying the solution, the acid, $\text{CN}\cdot\text{CH}_2\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, separates; it crystallises from water in large prisms, and melts at 142° with evolution of carbon dioxide, being converted into a substance having the formula $(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_x$, which crystallises from glacial acid in small, yellow needles having no definite melting-point; on distillation, it gives rise to the compound, $\text{CN}\cdot\text{CH}_2\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$, separating from absolute alcohol in large prisms melting at 181° and boiling at 208° under 25 m.m. pressure. The same substance is produced quantitatively if the ammonium salt of the acid melting at 142° is distilled under diminished pressure.

Concentrated aqueous potash hydrolyses the substances melting at 53° and 142°, forming malonic acid; the compound melting at 181°, when similarly treated, yields malonic and acetic acids.

When the sodium compound of the condensation product is heated directly with methyl iodide, the methyl compound, $\text{CN}\cdot\text{CHMe}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ is produced; it crystallises from dilute alcohol in small prisms, melts at 63°, and boils without decomposition at 220° under 20 m.m. pressure. With sodium carbonate, the acid, $\text{CN}\cdot\text{CHMe}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, is produced; it crystallises from water in glistening plates, melts at 145° with evolution of carbon dioxide, and becomes converted into a compound, $(\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2)_x$, having no definite melting-point, but which, on distillation, is converted into the substance, $\text{CN}\cdot\text{CHMe}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$, crystallising from absolute alcohol in small prisms, and melting at 121°. The same substance is produced when the acid melting at 145° is boiled for some time with sodium carbonate solution, or when its ammonium salt is distilled. The substances melting at 63° and at 145° give, on hydrolysis with aqueous caustic potash, malonic and methylmalonic acids; the compound melting at 121° yields methylmalonic and acetic acids.

When the sodium compound of the condensation product is treated directly with ethyl iodide, it is converted into the ethyl compound, $\text{CN}\cdot\text{CHEt}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, which crystallises from dilute alcohol in prisms, melts at 68°, and boils without decomposition at 215° under 20 m.m. pressure. With sodium carbonate it yields the acid, $\text{CN}\cdot\text{CHEt}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, which crystallises from water and melts at 153° with evolution of carbon dioxide, and becomes converted into an infusible substance having the formula $(\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2)_x$. The latter compound, on distillation, gives rise to the substance $\text{CN}\cdot\text{CHEt}\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$, which crystallises from absolute alcohol in small plates melting at 115°.

Complete hydrolysis of the above-mentioned substances melting at 68° and 153° gives rise to malonic and ethylmalonic acids; the compound melting at 115° yields ethylmalonic and acetic acids.

When the substance melting at 53° is treated with excess of sodium ethoxide and methyl iodide, it is converted into the trimethyl compound, $\text{CN}\cdot\text{C}(\text{Me})_2\cdot\text{HC}(\text{OEt})\cdot\text{O}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$, which crystallises from dilute alcohol in small needles and melts at 120°. Complete hydrolysis of this substance with aqueous potash gives rise to methylmalonic and dimethylmalonic acids.

The action of acidic hydrolytic agents on these substances, and the condition governing the formation of similar condensation products from substituted ethyl cyanoacetates, is under investigation.

153. "The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic." By W. T. COOKE.

Engel (*Comptes Rendus*, 1883, xcvi., 1314) states that amorphous arsenic is unaltered in moist air, whilst the crystalline modification oxidises rapidly. The author's experiments were made with the view of ascertaining:—(1) Whether water alone had any action on either variety; (2) whether the action, if any, was increased by the presence of caustic soda; (3) and whether, in the presence of air, the crystalline variety dissolved to a greater extent in caustic soda solution than in water.

Amorphous Arsenic.—The operations were carried out entirely in an inert atmosphere, the gas employed being either carbon dioxide or hydrogen, according as water or caustic soda solution was used. The main part of the apparatus consisted of two boiling tubes provided with condensers, and also with tubes for the introduction of the gas. Hydrogen arsenide was passed into one carefully dried boiling-tube, so that arsenic was deposited on warming. The water or caustic soda solution contained in the other tube was freed from air by boiling and by passing through it a current of hydrogen or carbon dioxide. The pressure of the gas in the apparatus was then used to force over the solution into the tube containing the arsenic, after any remaining hydrogen arsenide had been expelled. The solution could then be boiled in contact with the arsenic for any desired time, and finally drawn off through an asbestos filter. The arsenic in the filtrate was usually estimated by titrating with iodine solution.

The following results were obtained, using 125 c.c. of distilled water:—

Time of boiling, in hours.	Weight of dissolved arsenic, in grms.
2.5	0.0020
1.5	0.0009
2.5	0.0004
8	0.0034
4	0.0013
6	0.0016

In the absence of air, the action of water on amorphous arsenic is thus seen to be very slight. When air was aspirated through the boiling water for six and one-sixth hours in contact with the amorphous arsenic, only 0.0010 grm. of the element was dissolved, hence the presence of air has no effect.

In the absence of air, the effect of dilute caustic soda solutions was slightly greater than that of water, and the action increases with the concentration of the alkali. Moreover, the action is not influenced by the presence of air.

Concentration.	In the absence of air.		In the presence of air.	
	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.
N/100	1.5	0.0022	2.75	0.0014
	5.3	0.0026	6.0	0.0014
N/50	3.5	0.0021	2.5	0.0038
	6.0	0.0020	6.0	0.0010
N/25	6.0	0.0038	6.0	0.0046
			6.0	0.0014

Crystalline Arsenic.—In this case, the boiling tube was provided with a side tubulure, through which the crystalline arsenic could be introduced. The arsenic was powdered and introduced into the apparatus as quickly as possible on account of the readiness with which the finely-divided element undergoes oxidation. The volume of liquid used was 50 c.c. When distilled water was used and air excluded, about 0.0025 grm. of arsenic dissolved in one-and-a-quarter to one-and-a-half hours.

With distilled water in presence of air, about 0.0233 grm. of arsenic dissolved in one-and-a-quarter hours. Hence the presence of air greatly increases the action in the case of the crystalline modification of the element. The fol-

lowing results obtained with caustic soda show that the alkali does not materially increase the action.

Concentration.	In the absence of air.		In the presence of air.	
	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.
N/100	6	0.0025	6	0.0712
N/50	6	0.0016	6	0.0797
N/25	6	0.0030	6	0.0267
	6	0.0017		

By estimating the dissolved arsenic by the iodometric and gravimetric methods, it was found to be entirely in the form of arsenious acid.

The results seem to show that water, either alone or in the presence of caustic soda, has practically no action on arsenic. In the presence of air, however, direct oxidation takes place. If water is concerned in the oxidation, the formation of hydrogen arsenide might be anticipated: $2\text{As} + 3\text{H}_2\text{O} = \text{As}_2\text{O}_3 + 6\text{H}$, $2\text{As} + 6\text{H} = 2\text{AsH}_3$, but this gas was never found in the foregoing experiments.

Th. Panzer (*Chem. Centr.*, 1903, ii., 821), has also shown that the oxidation of arsenic in moist air is due, not to the decomposition of water, but to the intervention of free oxygen.

154. "Note on a Double Chloride of Molybdenum and Potassium." By G. G. HENDERSON.

According to Berzelius (*Poggendorff's Annalen*, 1826, vi., 331, 339; vii., 261), a chloride of molybdenum and potassium is obtained when the black liquid produced by the action of potassium amalgam on a solution of molybdenum pentachloride is evaporated to the crystallising point, and is described as a black efflorescent salt, which, when re-dissolved in water, leaves a black powder, probably a basic salt.

A definite double chloride of molybdenum and potassium, having the formula $3\text{KCl} \cdot \text{MoCl}_3 \cdot 2\text{H}_2\text{O}$, has been prepared in the following manner:—Potassium amalgam was added, in small quantities at a time, to a solution of molybdic acid in excess of hydrochloric acid until the liquid had acquired a purple-black colour. The solution was concentrated and saturated with gaseous hydrochloric acid, when successive crops of crystals were obtained; the first was composed of potassium chloride alone, the second of a mixture of potassium chloride with red crystals of the double salt, and the third of the double salt alone. The red crystals were collected, washed with fuming hydrochloric acid, dried by pressure between folds of filter-paper, and analysed with the following result:—

Found: Mo = 21.39, Cl = 45.46, H_2O = 7.47.

$3\text{KCl} \cdot \text{MoCl}_3 \cdot 2\text{H}_2\text{O}$ requires Mo = 20.92, Cl = 45.80, H_2O = 7.80 per cent.

The new salt, which crystallises in garnet-red prisms, is fairly easily soluble in cold water, without any apparent decomposition, giving a deep red solution. In the dry state the salt is quite stable, but it decomposes in aqueous solution, slowly in the cold, but quickly on boiling; this decomposition is prevented by the presence of hydrochloric acid. The salt is dissolved to a small extent, by concentrated hydrochloric acid, which then acquires a deep red colour.

When a solution of molybdic acid in hydrochloric acid was reduced in a similar manner by sodium amalgam, a few red crystals were obtained, very similar in appearance to those of the potassium salt; they probably consisted of the corresponding double chloride of molybdenum and sodium, but were not analysed on account of the difficulty of freeing them from admixed sodium chloride.

An attempt was made to prepare the potassium salt by adding potassium chloride to a concentrated solution of molybdic hydroxide, $\text{Mo}(\text{OH})_3$, in hydrochloric acid, and subsequent saturation of the liquid with gaseous hydrochloric acid, but in this case the brilliant green crystals of the compound $2\text{KCl} \cdot \text{MoOCl}_3 \cdot 2\text{H}_2\text{O}$, which has been pre-

pared previously, but in a different manner, by Nordenskjöld (*Ber.*, 1901, xxxiv., 1572), were produced instead of the expected double chloride. It was found that the same green crystals could be prepared by the action of potassium amalgam on a solution of molybdic acid in hydrochloric acid, if the potassium was added in smaller quantity than is necessary for the production of the red double chloride, and also that the green salt could be converted into the red salt by reducing its hydrochloric acid solution with potassium amalgam.

155. "The Action of Benzamidine on Olefinic β -Diketones." By S. RUHEMANN.

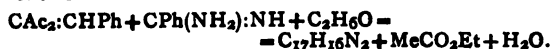
The author showed that hydrogen chloride reacts with a mixture of *m*-nitrobenzaldehyde and a β -diketone to form a *m*-nitrobenzylidenediketone, instead of giving rise to the additive product. Thus, *m*-nitrobenzaldehyde and acetylacetone furnish *m*-nitrobenzylidenediacetylacetone, $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}_6\text{H}_5$, melting at $101-102^\circ$. The yield of *m*-nitrobenzylidenediacetylacetone, —



(*m. p.* $111-112^\circ$), is very small, owing to the ease with which it is decomposed by acids. One of the products of the decomposition which has been isolated is *m*-nitrobenzylidenediacetophenone, $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_5$ (*m. p.* 145°).

m-Nitrobenzylidene- β -diketones are also produced by the action of piperidine on the dry mixture of the aldehyde and the diketone. But in alcoholic solution the saturated tetraketone is formed, such as *m*-nitrobenzylidenetetrakisbenzoylaceton, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{C}_6\text{H}_5$ (*m. p.* $229-230^\circ$).

Benzamidine reacts with benzylidenediacetylacetone, $\text{PhCO}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{Ph})\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}_6\text{H}_5$, at the ordinary temperature to form an additive compound (*m. p.* 132°), the constitution of which is $\text{NH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CPh}(\text{OH})\cdot\text{C}(\text{CH}_3)_2\cdot\text{CHPh}$, because the compound is decomposed by dilute hydrochloric acid, giving rise to dibenzamide. Similar additive products with benzamidine are formed from the other olefinic β -diketones; these, however, are changed when their alcoholic solutions are heated on the water-bath. Thus, sodium ethoxide and benzylidenediacetylacetone react with benzamidine at 100° as follows:—



The compound $\text{C}_{17}\text{H}_{16}\text{N}_2$ (*m. p.* $149-150^\circ$) is most probably dihydrodiphenylmethylpyrimidine, —



Benzamidine and *m*-nitrobenzylidenediacetylacetone interact differently, since *m*-nitrophenylphenylmethylpyrimidine, $\text{N} < \begin{matrix} \text{CPh} \\ \text{CMe}\cdot\text{CH} \end{matrix} = \text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*m. p.* $137-138^\circ$), is formed, instead of the corresponding dihydropyrimidine. The olefinic monoketone, benzylidenedesoxybenzoin, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CHPh}$, does not condense with benzamidine, and the action of hydrogen chloride on the mixture of *m*-nitrobenzaldehyde and desoxybenzoin proceeds in the same way as when benzaldehyde is used, and yields $\text{C}_6\text{H}_5\cdot\text{CHPh}\cdot\text{CHCl}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*m. p.* $166-167^\circ$).

156. "Dissociation Constants of Trimethylenedicarboxylic Acids." By W. A. BONE and C. H. G. SPANKLING.

In connection with the work on methylenedimethylsuccinic acid, it became necessary to determine the dissociation constants of some trimethylenedicarboxylic acids, since no data with respect to them were available. The following numbers were obtained:—

	K_{25°
Tetramethylenedicarboxylic acid	0.00171
Trimethylene-1 : 1-dicarboxylic acid	2.08
cis-Trimethylene-1 : 2-dicarboxylic acid	0.042
trans-Trimethylene-1 : 2-dicarboxylic acid	0.0215

A comparison of these values with those of the corresponding open chain saturated acids containing two

additional hydrogen atoms indicates that the formation of a trimethylene ring increases the constant, this effect being particularly noticeable in the succinic series.

157. "The Elimination of Hydrogen Bromide from Bromo-*gem*-dimethylsuccinic Acid and from Bromo-trimethylsuccinic Anhydride." By W. A. BONE and H. HENSTOCK.

Bromo-*gem*-dimethylsuccinic acid (*m. p.* 140°) is readily prepared by heating *gem*-dimethylsuccinic acid with the calculated quantity of dry bromine in sealed tubes at $130-140^\circ$; when heated with re-distilled diethyl aniline at 130° , carbon dioxide is freely evolved, hydrogen bromide is eliminated, and *neo*-tetramethyldihydromuconic acid is formed in the following manner:—



The new acid is obtained in well-defined transparent prismatic forms melting at 70° ; it is extremely soluble in the ordinary organic solvents with the exception of light petroleum; its aqueous solutions immediately decolorise alkaline permanganate with formation of the *dihydroxy*-acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, which melts at $129-130^\circ$. The dissociation constant of the tetrahydromuconic acid is $K_{25^\circ} = 0.001684$. The acid distils unchanged under the ordinary pressure, but when boiled with acetic anhydride it yields its own liquid anhydride.

In view of Paolini's observation (*Gazzetta*, 1900, xxx., [2], 497) that ethyl dimethyltrimethylenedicarboxylate is the product of the action of phosphorus pentachloride upon ethyl hydroxytrimethylsuccinate, the authors have repeated the work of Bone and Sprankling on the action of diethyl aniline on bromotrimethylsuccinic anhydride (*Trans.*, 1902, lxxxi., 50), and by a study of the physical properties of the resultant acid, $\text{C}_7\text{H}_{10}\text{O}_4$, have fully confirmed the previous conclusion that it is *methylenedimethylsuccinic acid*, $\text{CH}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. This acid melts at 142° , has a dissociation constant $K_{25^\circ} = 0.01597$, and gives an insoluble calcium salt. Determinations of the refractive power and magnetic rotation of diethyl methylenedimethylsuccinate, made by Dr. W. H. Perkin, sen., fully support the argument in favour of the unsaturated character as against the "trimethylene" configuration of the foregoing acid.

PHYSICAL SOCIETY.

Ordinary Meeting, November 27, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

MR. HORACE DARWIN exhibited an Electric Thermostat.

The thermostat shown at the meeting was made for Lord Berkeley, and is similar to one made for the spectrograph of the 24-inch refractor of the Royal Observatory, Cape of Good Hope. The vessel, the temperature of which is to be maintained constant, is surrounded by oil contained in a bath. In the oil are placed two heating coils, through which electric currents pass. By automatically controlling these currents, the temperature of the oil—and consequently of the inner vessel—is kept very nearly constant. The control is effected by means of a Wheatstone bridge in the outer oil-bath. This bridge has two opposite arms of copper and two of manganin, so that it is only balanced at some definite temperature. Its deviations from balance affect the position of a long horizontal boom attached to the suspended coil of a galvanometer. The position of the boom determines the greater or less descent of a "hit or miss" arm which is periodically raised by a rotating cam, and can only fall to its lowest position when the galvanometer-boom is to one side and allows it to pass; this position of the boom corresponds to a fall of temperature of the controlling-bridge. Thus the position of the "hit or miss" arm at its lowest position depends on the temperature, and it is the variation of this position

which regulates the amount of current passing through the heating-coils. When the "hit or miss" arm is at its highest position the galvanometer-boom is absolutely free to move to its position of equilibrium. We may call the two coils the intermittent and the permanent heating-coils. At every rotation of the cam the "hit or miss" arm is lowered, and if it passes the galvanometer-boom a key is closed and a current passes through the intermittent heating-coil. Thus the frequency of the intermittent current depends on the temperature of the oil-bath. The duration of the time that the key is closed also varies—it may be long or very short. Every time the key is closed a movement takes place which increases the duration of the next closure of the key. The arrangement of the mechanism is such that when the temperature is steady the "hit or miss" arm will pass the galvanometer-boom as many times as it is stopped by it in a given time. The current passing through the permanent heating-coil is also automatically regulated; if there is not enough heat passing into the oil this current is gradually increased. This is done by cutting out resistance-coils which are in series with the permanent heating-coils. The cam which moves the "hit or miss" arm is driven by a worm gear and any suitable motor, and the oil is kept thoroughly stirred by a fan.

Mr. W. C. D. WHETHAM asked what accuracy was aimed at in the instrument.

Mr. A. P. TROTTER said that the use of thermostats would become more and more important with the perfection of thermometers. It was possible to keep a temperature constant within $1/100^\circ$ C., but it was very difficult to determine the temperature to that degree of accuracy. In high-class resistance measurements with a Carey Foster bridge one of the greatest difficulties was with regard to the temperature, which must not only be constant, but also capable of exact determination. In the constant-temperature room at the Board of Trade Standardising Laboratory the temperature varied by less than $1/10^\circ$ C. from day to day, and he would like to know the greatest accuracy obtainable with ordinary devices in such a room before considering the introduction of the complicated instrument shown to the meeting.

The CHAIRMAN expressed his interest in the author's communication, and said he had recently been trying to solve a somewhat similar problem by making use of a horizontal boom, attached to the suspended coil of a galvanometer, for making and breaking a current. His object was to regulate a current of the order of 50 amperes. Dr. Glazebrook asked if it was desirable or important to utilise all the adjustments in the instrument.

The AUTHOR, replying to Mr. Whetham, said the instrument had been made as sensitive as possible, but he was not aware within what limits it would maintain the temperature of the bath. The thermostat supplied to the Cape Observatory was capable of keeping the temperature within $1/100^\circ$ C. for a period of eight hours. In reply to the Chairman, he said that when working with small variations of the external temperature it might be possible to dispense with one or other of the adjustments; but when the external variations were large, it was necessary at times to supply a large quantity of heat to the oil-bath, and in order to do this effectually he thought all the adjustments of the instrument were desirable.

A paper "On the Occurrence of Cavitation in Lubrication" was read by Mr. S. SKINNER.

The experiments described in the paper arose from an observation made when determining the refractive index of a liquid by means of Newton's rings. As Newton showed the rings can be obtained when a liquid is run into the space between the lenses. If when the liquid has been introduced the upper lens be rolled on the lower, the observer sees following the central dark spot a crescent-shaped space, very bright provided the illumination be sufficiently oblique. This is a vacuous or vapour-filled space, for when the motion of rolling ceases the liquid flows into the space and completely fills it. The inflow of the liquid depends in some way on the viscosity, and the

effects are more pronounced when a more viscous liquid is used. The most convenient mode of observation is to use a deeply coloured liquid, and to look at the space by transmitted light. The author has found that a convenient liquid is a strong solution of fuchsin in glycerin. This red solution is so deeply coloured that even up to the point where the lenses are nearest some colour shows, and light is only brightly transmitted at the place where there is a break in the liquid. The cavities which are formed must be produced either by splitting the liquid itself, or by tearing the liquid from the glass surface. The effect may be described as a case of "cavitation." Some experiments were made to imitate the actual case of a fully lubricated axle rotating under a bearing. For this purpose, a thick disk with its edge worked to a spherical surface of curvature equal to the radius of the disk, mounted on an axle, was arranged so that the lower part of the disk dipped into an oil-bath, whilst a flat plate of glass rested on the upper edge of the disk. As the disk rotated oil was carried round, so that the point of contact of the disk and plate was maintained copiously lubricated. The disk represented the axle and the plate the bearing on it. What happened on rotation could be observed by looking through the glass plate with a magnifying-glass. It was seen that during motion a cavity was formed on the side where the edge of the disk was moving away from the plate. The size of the cavity depended on the rate of rotation. In ball-bearings completely immersed in oil, the experiments showed that there must be a small cavity near the point of nearest approach of each ball to its neighbour, and also to the surface on which it is running. As the friction of the bearing is the viscous friction of the oil, it follows that the friction must be considerably reduced by the formation of these cavities which are filled with relatively non-viscous vapour. The high lubricating property of oils owes its origin not only to their superior viscosity, but also, possibly, to the facility with which cavities may be formed in them.

The author illustrated his paper by a series of experiments showing cavitation produced by rolling lenses on plates.

Prof. J. D. EVERETT said it was interesting to note that cavitation had been observed and correctly explained by Newton. He (Prof. Everett) mentioned that a similar phenomenon was exhibited by a steam-roller working on mud, and gave an explanation of the production of pressure and tension respectively in the liquid near the contact of the roller and the mud. If the mud were sufficiently viscid cavitation might occur behind the roller.

Mr. W. A. PRICE said that the observations of the author could not fail to be of interest to engineers. He asked to what extent cavitation was going on in an ordinary round bearing or in the slide-valve of a locomotive, and suggested that the views of engineers upon the subject of lubrication might require considerable modification in the light of the present paper.

Mr. C. V. BOYS expressed his interest in the paper and the experiments shown by the author. He said that like Mr. Price he had been thinking of the influence of cavitation upon machine bearings, but unlike him he had not come to the conclusion that our ideas on the subject should be changed. In the author's experiments cavitation was produced by the approach of two surfaces on one side of their line of contact and their recession on the other side. In the case of a cylindrical bearing the space between the shaft and journal was believed to be completely filled with oil, and if the shaft were truly concentric there would be neither approach nor recession. He thought that in the case of any cylindrical bearing the rate of approach and recession would never be great enough to produce cavitation. The case of ball-bearings, when using a thick lubricant, was different, and cavitation might occur. If it did it would occur behind the point of contact, and although the production of cavitation involved a loss of energy, he questioned whether it did any appreciable harm. Mr. Boys referred to the dendritic patterns formed, when mixing paints, by lifting the muller from the plate, and

suggested that their formation was a phenomenon of the same kind as cavitation.

Mr. R. APPLEYARD said there were two distinct cases to be considered:—(1) A wheel on a plane, and (2) a shaft in its bearings. He agreed with Mr. Boys that the cavitation occurred behind the point of contact, and did not matter in the case of a ball-bearing. But if cavitation occurred in a cylindrical bearing, the cavity would form between the two surfaces which were next coming into contact. If the surfaces were smooth little harm would ensue, but if they were rough the occurrence of cavitation would be detrimental, for it would result in direct contact.

Dr. A. GRIFFITHS asked the author if cavitation in lubrication was supposed to be an advantage or disadvantage.

Mr. SKINNER, replying to Mr. Boys, suggested the construction of glass bearings to determine whether cavitation occurred in cylindrical shafts. He thought that cavitation in lubrication was an advantage as a rule, because spaces formerly filled with viscous material were then filled with something with small viscosity.

Prof. R. THRELFALL then exhibited and described the following instruments which he has used in the testing of electric generators by air calorimetry:—

1. A Hot-wire Voltmeter accurate to 1/100th volt. The wire in this instrument is very fine, and special precautions are taken to keep the tension on it constant, so that the elongation measured is due only to the expansion of the wire caused by the heating effect of the current.

2. A Pitot Tube for the measurement of air velocity, the velocity being proportional to the square root of the pressure produced in the tube.

3. A Manometer for determining pressure-differences in Pitot tubes with accuracy. This consists essentially of two bottles containing coloured water, which are connected by a syphon, and the air-space of each bottle is put in communication with its appropriate tube. The readings are taken by setting a pair of needle-points just to touch the liquid surface, and then measuring how they differ in level by micrometer-screws, or by calliper suitable jaws. The instrument is reliable to 0.01 m.m. of water-pressure.

4. A Multiplying Pressure-gauge in which the motion of a float or ball is used to operate a finger moving round a dial. The dial is divided in such a manner that the square roots of the pressure-differences are read off. Air-velocities are therefore given directly.

Mr. DUDDELL, referring to the voltmeter exhibited, asked if there was any trouble with regard to the temperature variation of the resistance of the wire. In using the instrument with large alternating currents it was necessary to use a standard shunt, and difficulties then arose because of the fact that the self-induction of a shunt, formed of straight bars, and capable of carrying the necessary current, was comparable with its resistance. It might be possible to get a satisfactory shunt by doubling the bars upon themselves to reduce the self-induction.

Prof. THRELFALL said that there was no difficulty with regard to changes in temperature of the room because they only altered the zero of the instrument. Referring to the possibility of constructing a low-resistance standard shunt, he said he had calculated the self-induction of the bars forming his shunts, and had come to the conclusion that it was negligible in his experiments. Experimentally he had found that it could not produce an error of 1 per cent. It might be possible to so design a shunt that the mutual induction of its parts would balance the self-induction to a certain extent.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. Andrew Carnegie, Mr. J. S. Curgenven, Dr. J. Emerson Reynolds, and Mr. R. Wissmann were elected Members.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali. By GEORGE LUNGE, Ph.D. Third Edition, Revised and Enlarged. Volume I., Parts I. and II., Sulphuric Acid. London: Gurney and Jackson. 1903.

ALTHOUGH only some seven years have elapsed since the appearance of the Appendix to the Second Edition of this work, the rapid development of the subjects of which it treats, especially as regards the manufacture of sulphuric anhydride, has already made it desirable to issue a third edition, which has been re-written to a large extent, and thus, while preserving the essential features of the earlier editions, records the most recent advances and changes which have been made. Certain alterations and omissions have necessarily been made to allow of the inclusion of a large amount of new matter, and many fresh illustrations; while some drawings which appeared in the second edition have not been repeated in order to save space. As the work stands in its present form it undoubtedly represents the most complete treatise of its nature in existence, and it may rightly be regarded as quite indispensable as a work of reference.

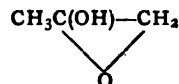
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 19, November 9, 1903.

Conditions of Separation of Iodine in the form of Cuprous Iodide from a Mixture of Chlorides, Bromides, and Alkaline Iodides.—H. Baubigny and P. Rivals.—The simplest method of separating iodine from a mixture of chlorides, bromides, and alkaline iodides is to precipitate the iodine by the simple addition of CuSO_4 , and this is really the most effectual if the operation takes place in presence of excess of chlorides and bromides. In no case have the authors obtained an exact result by the method of evaporation *in vacuo* of the liquor and of free iodine, for in this method it seems that after the rough estimation of the iodine remaining in the dry product perfect exactitude is not possible, because when the dry product is dissolved in water, a process which leaves the insoluble Cu_2I_2 , a little iodine always goes into solution, and in the form of a cuprous salt, giving a less weight than should be obtained; for example, in a series of experiments on a silver salt, 0.068 gm. AgI were obtained, instead of 0.069 gm., and 0.2742 gm. instead of 0.276 gm.

Action of Organo-magnesium Derivatives on Acetol and its Ether Salts.—André Kling.—The author has previously shown that acetol in solution can exist partially in the form of an ether oxide having the formula—



He now investigates what the constitution of this alcohol and its ethers is in an anhydrous state, and for this purpose he uses organo-magnesium derivatives. When compared with the changes taking place during the reaction of organo-magnesium compounds on epichlorhydrine or on ethylene oxide, he finds that anhydrous acetol or the anhydrous ether salts behave as ketonic compounds and not as internal ether oxide compounds.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brongh.

TUESDAY, 15th.—Society of Arts, 8. "The British Silk Industry," by Frank Warner.

WEDNESDAY, 16th.—Society of Arts, 8. "The Science of Taxation and Business," by Sir William Henry Preece, K.C.B., F.R.S.

Chemical, 530. "Relative Strengths of the Fixed Bases and of Ammonia as Measured by the Reaction on Cotarnol," by J. J. Dobbie, A. Lauder, and C. K. Tinkler. "New Halogen Derivatives of Diphenyl and Dihydroxydiphenyl," by J. C. Cain. "Constitution of Nitric Peroxide" and "Sabatier's Nitrosodisulphonic Acid," by E. Divers. "Notes on some Natural Colouring Matters," by A. G. Perkin and E. Phipps. "Estimation of Methyl Alcohol in presence of Ethyl Alcohol," by T. E. Thorpe and J. Holmes.

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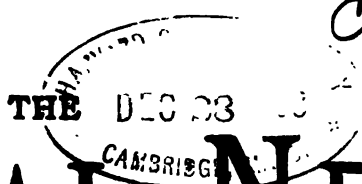
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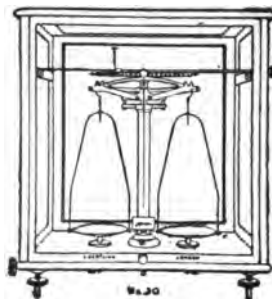
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2299.

AN EXACT SEPARATION OF CERTAIN OF THE RARE EARTHS.

By G. URBAIN and H. LACOMBE.

FRACTIONAL crystallisation of two salts which are not isomorphous can never result in the production of either the least soluble or the most abundant in a good state of purity. If the solution has a certain composition to start with, the two salts crystallise simultaneously, forming a eutectic mixture, and never, however often crystallisation is repeated, can they be absolutely separated.

In the case of isomorphous salts the phenomena are quite different. By a series of fractional crystallisations properly carried out a mixture of isomorphous salts can be separated into its constituents in the order of their solubility.

After a sufficient number of fractionations each one will be obtained pure. It will also be noticed, indeed, that in a mixture of isomorphous salts a more soluble member of the series diminishes the solubility of a less soluble member. The true solubility of each salt when in a pure state is profoundly modified by the presence in the solution of an homologous salt of the series in such a manner that during separation by fractional crystallisation the individual solubility of each salt appears of less importance than the tendency of the salts to substitute each other in the crystalline deposit.

It is this tendency to substitute one another in the deposit which enables us in certain cases to separate the least soluble salts in a pure state from those which accumulate in the mother-liquor. So exact is the separation that even the most delicate tests fail to discover a trace of the least soluble salts at the opposite end of the fractionation.

To separate elements whose properties vary very slightly from one member to another of the series, as in the family of the rare earths, this remarkable property of isomorphous salts can be utilised. It is by crystallisations of relatively very soluble salts that the best results are obtained. Double salts, where the differences of solubility between the members are usually greater than those of simple salts, can be most conveniently separated by this method. Fractionation methods are still, and likely to remain for a long time, the only means of which allow of the separation of the rare earths among themselves. Cerium alone has a series of stable higher oxides, which can always be utilised for its separation from other rare earths.

In all cases the great difficulty of fractional methods for the separation of the rare earths is the presence of intermediate portions, which, though they can often be considerably reduced, can never disappear altogether, except in the following case:—When an element, usually separated with no difficulty from the rare earths, presents a case of isomorphism. Also if the solubility of the salt of the common element is intermediate between that of the two members of the series.

An example of such a case is the isomorphism of double nitrate of magnesium and bismuth with the double nitrates of magnesium and the rare earths (G. Urbain and H. Lacombe, *Comptes Rendus*, 1903, vol. cxxxvii., p. 568). In a preliminary examination we compared this bismuth compound with the corresponding salts of the samarium-gadolinium group, and we thought at the beginning of our researches that if we added to the magnesium nitrates of these earths, whose fractionation was described by Demarçay (*Comptes Rendus*, 1896, vol. cxxx., p. 1019; 1901, vol. cxxxii., p. 1484; 1901, vol. cxxxiii., p. 1469) with such brilliant results, a certain proportion of bismuth magnesium nitrate, the element

bismuth will, little by little, be inserted between the two rare earths, gradually separating the elements. A simple precipitation by sulphuretted hydrogen will then eliminate the bismuth, and we should obtain a rigorous separation in the rare earth series for the first time.

Experiment has fully confirmed our prediction, and the results obtained have surpassed our expectations.

We have fractionated in presence of magnesium nitrate (1) earths rich in samarium, (2) earths rich in gadolinium. In both cases we have added a considerable quantity of bismuth magnesium nitrate to the rare earth magnesium nitrates.

After 35 series of fractionations, each resulting in 10 fractions, we have made the following observations:—Neodymium concentrates at one end, and is only mixed with bismuth.

Samarium comes next. The oxide extracted from fraction 2 shows the slight yellow colouration characteristic of samarium. This colouration diminishes in the following fractions. In the same way the yellow colouration and the absorption spectra of the solution decrease from one fraction to the next. The proportion of rare earths decreases at the same time as the proportion of bismuth increases. In the first experiment with a substance rich in samarium the Fractions 11 and 12 contain no trace of rare earths. In the second experiment, when an earth containing very little samarium was used, Fractions 4, 5, and 6 contain only bismuth. In the following fractions the rare earths appear again, and their proportion increases up to the end of the series, whilst the proportion of bismuth decreases. The solutions show no absorption spectrum except the last fraction, when faint bands of dysprosium may be distinguished. The colour of the oxide starts from white gadolinia up to the last fraction, when the earth is brick-red.

These observations apparently show that bismuth inserts itself between samarium and gadolinium. We are less certain in our experiments on Demarçay's europium. To elucidate this latter point, we are experimenting with a kilogram of earths intermediate between samarium and holmium.—*Comptes Rendus*, November 16, 1903, vol. cxxxvii., No. 20.

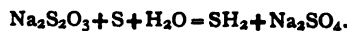
THE DECOMPOSITION OF CRYSTALLISED SODIUM THIOSULPHATE BY HEAT.

By ARTHUR JAKUES.

WHEN gradually heated, crystallised sodium thiosulphate melts in its own water at 45°, and gradually loses more or less of its moisture as the temperature rises to 215° C., when the whole of the water is driven off. At 220° it is decomposed, with liberation of sulphur.

The author, however, finds that when the crystallised salt is quickly heated in a test-tube it is decomposed near the hot wall of the tube while the water is still being given off from the mass; sulphuretted hydrogen is formed in considerable quantity.

It is evident that the hydrogen present in the SH₂ can only have come out of the water, so that the nascent sulphur, together with the reducing influence of the sodium sulphite formed in the decomposition, has been sufficient to break up the water at the temperature of the mixture, thus,—



Sulphur, sodium sulphite, and sodium sulphate are present in the residue.

It is noteworthy that no sulphur dioxide is given off; so that the presence of the sodium sulphite appears to be necessary for the action to go on, as otherwise the oxygen out of the water would probably unite with the free sulphur which is present in the residue, forming SO₂. (This would, of course, destroy the SH₂).

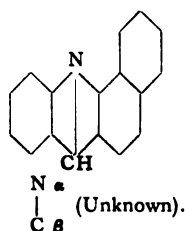
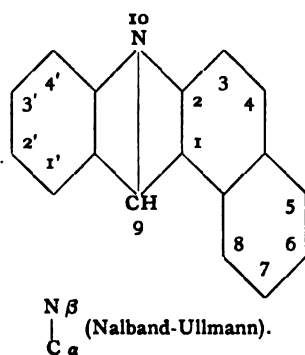
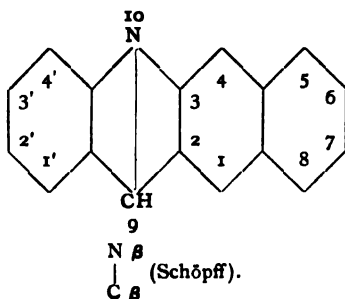
* Pape, Roscoe and Schorlemmer's "Treatise on Chemistry."

ON ACRIDINES.*

By ALFRED SENIER, Ph.D.,
Professor of Chemistry in Queen's College, Galway.
(Concluded from p. 286).

VI. Phenonaphthacridines.

1. Possible Isomeric Types:—



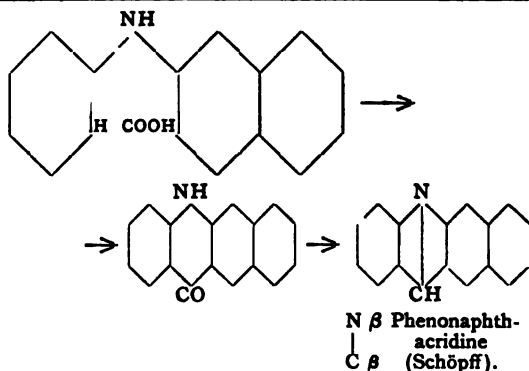
The acridine of this type has not yet been obtained, but a corresponding dihydroxyacridone was prepared by Lagodzinski and Hardine (see below).

The naming of the isomerides is a modification of that which I have proposed for the naphthacridines; the numbering is that employed by Ullmann (*Ber.*, 1894, xxvii., 3066).

2. Formation and Constitution:—

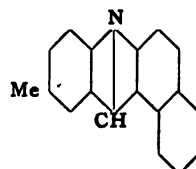
- i. The diamine and acid reaction was that first employed. From phenyl-β-naphthylamine and benzoic acid Claus and Richter (*Ber.*, 1883,

xvii., 1590) prepared a phenyl-β-phenonaphthacridine, and Schöppf (*Ber.*, 1893, xxvi., 2589) by a modification of the method, using 2:3-anilidonaphthoic acid, obtained the corresponding acridone and acridine, thus:—



- ii. Replacement of one of the naphthalene groups in dihydroxydi-α-naphthyl methane by *p*-toluidine, and subsequent condensation was effected by Ullmann and Naef (*Ber.*, 1900, xxxiii., 905), forming the "leuco" base, phenonaphthacridine

dihydride, and by oxidation N β-2'-methyl-phenonaphthacridine:—



Numerous derivatives chiefly of the phenyl ring were prepared (Ullmann and Naef, *Ber.*, 1900, xxxiii., 912 and 2470; Ullmann and Marié, *Ber.*, 1901, xxxiv., 4320).

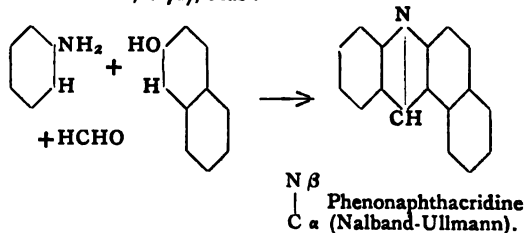
- iii. Further derivatives of N β phenonaphthacridine

were obtained by Ullmann and Naef (*Ber.*, 1900, xxxiii., 916) by replacement of one of the benzene rings in the tetra-amino-ditolylmethane by naphthalene and subsequent condensation.

- iv. A modified diamine and aldehyde reaction was also employed by Ullmann and Naef (*Ber.*, 1900, xxxiii., 908). *p*-Toluidine formaldehyde and

β-naphthol giving N β-2'-methyl-phenonaphthacridine. Methods based on this reaction were

patented by Ullmann (German Patents 117472, 118439, 123260). The type compound of these derivatives seems to have been first prepared by Nalband (Ullmann and Baezner, *Ber.*, 1902, xxxv., 2671), thus:—

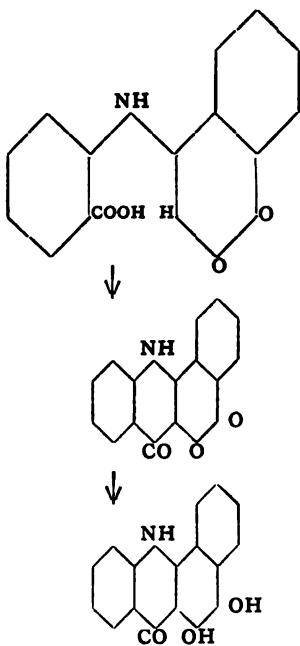


Numerous derivatives are described by Ullmann and his students (*Ber.*, 1901, xxxiv., 4317; 1902, xxxv., 316 and 326; *Journ. Chem. Soc. Abstracts*, 1903, lxxxiv., 447; German Patents 127586 and 128754).

* Abstract of a Paper read before the British Association (Section B), Southport Meeting, 1903.

By this method Lagodzinski and Hardine (*Ber.*, 1894, xxvii., 3068) obtained a dihydroxy-

acridone corresponding to the $\begin{array}{c} \text{N} \alpha \\ | \\ \text{C} \beta \end{array}$ type, thus:—



The remarkable readiness with which the acridine grouping is brought about is shown by the recent observation of Ullmann and Baezner (*Ber.*, 1902, xxxv., 2671) that the alcohol group may replace the aldehyde group in this method—that *o*-aminobenzyl, alcohol for example, condenses with β -naphthylamine to form the Nalband-Ullmann base, oxidation taking place during the experiment.

VII. New Acridines.

With the assistance of Miss Micklethwait I am now endeavouring to obtain new types of acridines. We are trying by the methylene diiodide and modified diamine method to condense diaminonaphtholenes to form ring of ring compounds; amino-anthracenes to obtain anthracridines, and by means of suitable amino-derivatives to prepare phenoanthracridines and naphthanthracridines. These experiments are in progress, but we are able to announce that in many of them promising fluorescent products have already resulted.

ARSENIDES OF COPPER.

By ALBERT GRANGER.

CHEMISTS who have studied the compounds of copper and arsenic have described a number of these bodies. Gehlen ("Handbuch der Anorganischen Chemie," 6th Edition, vol. iii., p. 702) has prepared a white substance with a metallic lustre, corresponding to the formula Cu_4As_6 , by heating a mixture of the two elements. Kane (*Pogg. Ann.*, vol. xlv., p. 471) obtained a black body which should be Cu_3As_2 by reacting with arseniuretted hydrogen on hot chloride of copper, or on sulphate of copper in solution. The reduction of arseniate of copper by cyanide of potassium gives the same body as shown by Descamps (*Comptes Rendus*,

vol. lxxxvi., p. 1023). The same worker obtained Cu_3As in a direct manner. These arsenides, Cu_3As_2 and Cu_3As , are produced in the form of metallic ingots, which lose arsenic when they are heated, and leave as residue a less arseniuretted metal, Cu_3As .

By re-melting the product of the reduction of sulphate of copper in solution by arsenic under a layer of boric acid, Descamps obtained Gehlen's arsenide, Cu_4As_2 ; he describes it as a crystalline body. Reinsch, by reacting with copper on an arsenious hydrochloric solution, isolated another arsenide, Cu_3As_2 , in the form of a grey precipitate.

In nature there are a certain number of minerals consisting of arsenide of copper. Dana ("The System of Mineralogy," 6th Edition, p. 44) describes domeykite, algodonite, and whitneyite, which are arsenides varying from Cu_3As to Cu_6As and Cu_2As . (Koenig (*Bull. de la Soc. Franç. de Mineralogie*, 1902, vol. xxv., pp. 266 and 362) has added to this list minerals found in the Mohawk mine at Keweenaw (Michigan), and which also contained cobalt and nickel. These arsenides consist of amorphous masses of which the colour varies from white to yellow, and have a metallic lustre.

I have endeavoured to obtain arsenides of copper by direct combination, but I have made use of an apparatus which enables me to avoid too great a superheating, the effect of which is to bring about the partial decomposition of the product formed.

In a glass tube traversing a sulphur bottle, and through which a current of carbonic acid passes, a porcelain boat filled with copper reduced by hydrogen is placed, and in front of it is another boat containing sublimed arsenic. Under these conditions the copper is attacked very easily, and by prolonging the reaction we obtain a well crystallised arsenide, Cu_3As_2 , which has the same composition as the body described by Reinsch, but which occurs in very distinct crystals, while the body already described was in the form of an amorphous powder. This arsenide is of a steel-grey colour in the form of octahedra combined with rhomboidal dodecahedra, having cube facets on their summits.

The density of these crystals is 7.56. They gradually become tarnished when exposed to the air, nitric acid dissolves them, and the oxidising agents, chlorine and bromine, attack them with ease.

The arsenide, Cu_4As_2 , corresponds to a phosphide of copper, Cu_3P_2 , that I have described already (*Bull. Soc. Chim.*, [3], vol. vii., p. 614; *Comptes Rendus*, vol. cxlii., p. 1041). It is similar in its chemical properties, but differs in crystalline form, the Cu_3P_2 being hexagonal. This phosphide is only formed at a higher temperature, about 900°. Like this body the arsenide is decomposed when heated to 1200°, only 20 per cent of arsenic remains. At a higher temperature than that obtained by boiling sulphur in an iron bottle we can still prepare a definite and well-crystallised arsenide of copper, but the operation becomes more delicate on account of the possibility of superheating. If, for any reason, the mass is not always kept in the presence of arsenical fumes, there is a loss of arsenic. Among the workers I have already quoted, Descamps obtained arseniuretted copper, the composition of which corresponded to Cu_3As . It is generally an arsenide of this character that we obtain if we proceed without sufficient precautions.

At the bottom of the porcelain boat we find a brilliant brittle ingot, which differs very little in composition from Cu_3As , if the temperature has not reached 900°. Below this temperature it is still possible to obtain the body Cu_3As_2 if we prolong the action of the arsenic.

The reaction is comparable with that by which we prepare Cu_3P_2 (*Ann. Chim. Phys.*, Series 7, vol. xiv., p. 60); after the apparatus has sufficiently cooled, we find a metallic ingot covered with crystals. There is a difference between these two bodies, and that is that the preparation of Cu_3P_2 is infinitely more delicate than that of Cu_3As_2 . It is only within very limited variations of temperature that the phosphite is formed, for below 1000° it

gives bodies containing more phosphorus than Cu_3P_2 , such as Cu_2P , Cu_3P_2 , while only a single arsenide, Cu_3As_2 , appears to be formed at this limit. I have not been able to obtain arsenides corresponding to the above mentioned phosphides richer in arsenic than Cu_3As_2 .

By a roundabout method, that is to say, by acting with chloride of arsenic on the metal, or with arsenic on chloride of copper, there is certainly an arsenide of copper formed, but it is no other than the body just described. Further, it is formed under the same conditions of temperature, and in the sulphur bottle the reaction of arsenic on chloride of copper can be easily brought about. This method of working offers no advantages on account of the corrosive action of the chloride of arsenic.

The analytical separation of copper and arsenic leads me to make a few remarks which may not be without value. The general method, that is to say, the separation of the two sulphides by means of sulphide of sodium, offers no advantages, as under these conditions the sulphide of copper is difficult to wash, and may pass through the filter. Fresenius pointed out that the precipitation of the copper in the presence of arsenic may be effected by means of sulphocyanate; in the present case I always found copper in the solution. The simplest method is to precipitate the arsenic in the state of ammonio-magnesian arseniate. The solution of the substance in nitric acid is peroxidised with a few crystals of chlorate of potassium. Neutralise with ammonia and add a sufficient quantity of this reagent to obtain a limpid solution, then precipitate with the magnesian solution.

The precipitate once separated, the wash-waters are evaporated to dryness, and the copper is estimated in the residue in the form of sulphide, after precipitation in the state of sulphide or of sulphocyanate, after expulsion of the ammonia.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

A PARTICULAR PROPERTY OF SOME HYDRATED SALTS.

By A. DE SCHULTEN.

A CONSIDERATION of the salts which form several hydrates shows that, as a general rule, by successive increases of temperature, the hydrate richest in water gives the lower hydrates. To take a few examples, I will mention that the sulphate of magnesium containing 12 molecules of water of crystallisation is transformed, even at a few degrees above freezing, into a sulphate containing 7 molecules; that at 52° this gives the salt containing 6 molecules, and that at 132° this latter forms the sulphate containing only one molecule of water (Gmelin, "Handbuch der Chemie"). The dimagnesian phosphate, $\text{HMgPO}_4 \cdot 7\text{H}_2\text{O}$, heated to 100° , gives the salt $\text{HMgPO}_4 \cdot 3\text{H}_2\text{O}$ (*Ibid.*) Carbonate of soda containing 10 molecules of water gives, while efflorescing at 12.5° , the salt containing 5 molecules of water, and the latter when heated to 38° gives the salt containing 1 molecule (*Ibid.*).

There are some series of hydrated salts which form an exception to this rule. All the hydrated salts being so many perfectly distinct compounds, the peculiarity in question is simply an individual property. Nevertheless, it appeared to be interesting to record it in the following well-established cases.

We know two hydrated double carbonates of lime and sodium: gaylussite, $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$, and pirssonite, $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$. Gaylussite loses the whole of its water at 100° . I have confirmed this fact with well-crystallised, artificial gaylussite prepared according to Fritzsche's method. The loss at 100° was found to be 30.30 per cent (gaylussite contains 30.41 per cent of water).

Pirssonite does not undergo any change at 100° , and it is only at a temperature of 130° that it loses the whole of its water. I have checked the accuracy of these facts by operating on artificially prepared pirssonite, made by the

method I have previously described (*Comptes Rendus*, 1896, vol. cxxii., p. 1023).

The artificial pirssonite used for this purpose was very well crystallised and extremely pure, as the following figures, obtained by analysis, show:—

	Found.	Calculated.
Na_2O	25.69	25.65
CaO	23.28	23.13
CO_2	36.21	36.34
H_2O	14.91	14.88
	100.09	100.00

Thus it is well established that gaylussite loses the whole of its water at a temperature at which pirssonite does not undergo any change.

During the course of my research on trimagnesian phosphate and arseniate (*Bull. Soc. Min.*, 1903, vol. xxvi., p. 81) I had occasion to observe that the phosphate, $\text{Mg}_3(\text{PO}_4)_2 + 22\text{H}_2\text{O}$, well-crystallised and pure, when heated to 100° , very quickly loses 18 molecules of water, and then very slowly loses more water, while artificial bobierite, $\text{Mg}_2(\text{PO}_4)_2 + 8\text{H}_2\text{O}$, also well crystallised and pure, does not undergo any alteration at 100° .

The crystallised arseniate, $\text{Mg}_3(\text{AsO}_4)_2 + 22\text{H}_2\text{O}$, loses 17 molecules of water very quickly at 100° , and then slowly a further quantity of water, while crystallised artificial hoernesite having the formula $\text{Mg}_3(\text{AsO}_4)_2 + 8\text{H}_2\text{O}$ does not change at all at 100° .

Thus it is shown that the trimagnesian phosphate and arseniate containing 22 molecules of water retain less than 4 and less than 5 molecules respectively at 100° , a temperature at which the arseniate and phosphate containing only 8 molecules of water do not experience any loss whatever.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

RELATIONS BETWEEN ATOMIC WEIGHTS.

By REGINALD J. HUGHES.

ATTEMPTS have often been made to find simple numerical relations between the atomic weights of elements in the same series. For instance, it has been pointed out that the atomic weights of Li, Na, K, Rb, and Cs are nearly in the proportion of 1, 3, 5, 11, and 17, taking 7.7 as the unit. Similarly, the elements in the beryllium and oxygen series have atomic weights which are roughly multiples of 8. But none of these methods give more than approximations which generally seem to imply a margin of error greater than is likely to occur in accurate modern determinations of atomic weight.

The following relations between the numerical values of this function for different elements approach more closely to the experimental values, and are, I believe, new:—

Let us suppose that elements are built up of aggregations of corpuscles, which tend to combine in groups according to a comparatively limited number of types, and that these types are the same as those of the compound radicles of our chemistry, which may, on this view, be termed elements of the next order. The types I shall consider at present are NH_4 , CN , CH , and NH . The first two, as is well known, are analogous to sodium and chlorine and their related elements. The group CH resembles in many ways triad nitrogen or phosphorus. This is especially shown in organic compounds, such as the pyridine bases, which are benzenes with CH replaced by N ; and the radicle NH behaves in several respects like a carbon atom. Stereochemical work has demonstrated that the four free valencies in the group NR can be typified as arranged in space exactly like those of the carbon atom tetrahedron, and that, conversely, the group CH may be replaced by N .

I must premise that I shall not attempt to explain the change in valency of the phosphorus group to pentad, or of copper to dyad. I believe that to be impossible under our

H .. 1'0075	Na .. 23'05	C .. 12'00	P .. 31'0	V .. 51'2	Cl .. 35'45
O .. 16'000	Cu .. 63'6	Si .. 28'4	As .. 75'0	Nb .. 94	Br .. 79'96
	Ag .. 107'93	Ti .. 48	Sb .. 119'9	Ta .. 183	I .. 126'86
	Au .. 197'2	Ge .. 72			
		Zr .. 90'6	Bi .. 208		

present method of regarding valencies. The annexed table shows the elements considered and the values of the atomic weights used, most of which are, I think, in accordance with the best observations.

Suppose $N_1 + 4H_1 = Na$, $N_1 + H_1 = C$, and $C_1 + N_1 = Cl$; calculating this out we get—

$H_1 = 3'683$, $N_1 = 8'317$, $C_1 = 27'133$, and $C_1 + H_1 = 30'816$, the accepted value for phosphorus being 31'0.

Now take $N_2 + 4H_2 = Cu$, $N_2 + H_2 = Si$, $C_2 + H_2 = As$; then $H_2 = 11'733$, $N_2 = 16'667$, $C_2 = 63'227$. Hence—

$$C_2 + N_2 = 79'894 = Br;$$

the experimental value is 79'96.

Similarly, if $N_3 + 4H_3 = Ag$, $N_3 + C_3 = I$, $C_3 + H_3 = Sb$; $H_3 = 20'194$, $N_3 = 27'154$, $C_3 = 99'706$; so that—

$$N_3 + H_3 = 47'348 = Ti.$$

The agreement is not quite so good, but the atomic weight of titanium is not very accurately known.

On examining the values found for C_1 , C_2 , and C_3 , it will be seen that—

$$\begin{aligned} C_1 &= 3 \times 9'0443 \\ C_2 &= 7 \times 9'0324 \\ C_3 &= 11 \times 9'0642 \end{aligned}$$

The values of C increase by a constant amount.

If these are really species of "carbon radicles," and if PH, AsH, &c., are also analogous to carbon, then the latter series might show the same numerical relationship; and this is the case.

$$\begin{aligned} PH &= 3 \times 10'669 \\ AsH &= 7 \times 10'858 \\ SbH &= 11 \times 10'992 \\ BiH &= 19 \times 11'000 \end{aligned}$$

I only claim that the numbers taken as units are approximately constant; they show evidence of a definite increase at a diminishing rate. There is a missing element at $15 \times 10'996$; this gives $X = 163'933$. Now $H_3 - H_2 = 8'461$ (see above), and $H_2 - H_1 = 8'050$. We may take as a hypothesis that the increase is always approximately 8. $24 + 3'7$ gives $H_4 = 27'7$. Subtracting from 163'933, we have

$$C_4 = 136'233 = 15 \times 9'082.$$

Moreover, H_5 will be about 35'7. Subtracting from Bi (208),—

$$C_5 = 172'3 = 19 \times 9'068.$$

We can now calculate the atomic weight of gold:—

$$N_5 + H_5 = Zr = 90'6;$$

so that—

$$N_5 = 54'9 \text{ and } N_5 + 4H_5 = Au = 197'7.$$

Using germanium in the same way (as $N_4 + H_4$), the missing element between silver and gold would have an atomic weight of 155'1.

The most analogous element to hydrogen in the halogen group is chlorine. PCl , $AsCl$, &c., might, on my theory, also be species of "carbon radicles," and the same series again appears, the unit being this time still more constant. The value of X is that obtained above.

$$\begin{aligned} PCl &= 3 \times 22'15 \\ AsCl &= 5 \times 22'09 \\ SbCl &= 7 \times 22'19 \\ XCl &= 9 \times 22'15 \\ BiCl &= 11 \times 22'13 \end{aligned}$$

The appearance of the multipliers 5 and 9 suggested an examination of the vanadium series. The atomic weights

of members of this group are, however, not known to a very high degree of accuracy.

$$\begin{aligned} VH &= 5 \times 10'44 & VCl &= 4 \times 21'66 \\ NbH &= 9 \times 10'56 & NbCl &= 6 \times 21'58 \\ TaH &= 17 \times 10'82 & TaCl &= 10 \times 21'84 \end{aligned}$$

It is difficult to believe that these relations can be all due to coincidence. The method should be capable of wide extension, so as to include eventually all the elements in the table, and also further analyse those whose structures have been tentatively described above. It must be noticed that I do not consider either the series H_1 , H_2 , &c., or N_1 , N_2 , &c., to increase by constant increments; but the series C_1 , C_2 , &c., does increase in an arithmetical progression, like the successive additions of CH_2 to an organic radicle.

Trinity College, Cambridge.

THE DETERMINATION OF POTASH IN FERTILISERS BY SUBSTITUTING MILK OF LIME FOR AMMONIA AND AMMONIUM OXALATE AS THE PRECIPITANT.*

By C. L. HARE.

THE Lindo-Gladding method for the determination of potash in fertilisers possesses one particularly objectionable feature: the evaporation and ignition of an aliquot with sulphuric acid for the purpose of expelling ammonia salts and destroying dissolved organic matter is a tedious process, and involves probable loss from sputtering during evaporation. A reliable modification which would exclude this feature would be highly desirable. At the Sixteenth Annual Meeting of the Association of Official Agricultural Chemists Mr. Ross presented a method based upon the use of barium carbonate as a precipitant for phosphates, iron, alumina, &c. He later suggested milk of lime as the precipitant, and the writer, in 1901, reported results obtained by collaborators on official methods for potash determination. The method employed is as follows:—

Weigh out 10 grms. of the sample and boil with about 350 c.c. of water for thirty minutes; while hot, add milk of lime till slightly alkaline. Cool, make up to 500 c.c. with water, and remove 50 c.c., corresponding to 1 gm. Acidify with hydrochloric acid, add platinum solution, and evaporate to soft dryness over water-bath. The residue is then washed with 80 per cent alcohol and ammonium chloride "wash," as in the Lindo-Gladding method.

In the case of fertilisers containing organic matter, treat 10 grms. of sample with dilute sulphuric acid (1:1) and incinerate; moisten ignited mass with dilute sulphuric acid (1:1), and heat to aid in removing from the dish; boil with 350 c.c. water, and proceed as before. The milk of lime precipitates all lime except that present as sulphate, and the solubility of the sulphate being only 1 in 500, the aliquot of 50 c.c. will contain only 0'1 gm. of that substance, an amount readily removed by the ammonium chloride wash-water, and insufficient to cause material trouble either when solution is made with water direct or after incineration with sulphuric acid.

The potassium platonic chloride crystallises well, and, after washing with alcohol, the salts of lime appear in light flakes, which require never more than six washings with ammonium chloride "wash" for complete removal.

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

TABLE I.—*Determination of Potash in Fertilisers containing no Organic Materials.*

(Solution by boiling sample with water).

Lime method. Per cent.	Lindo-Gladding method. Per cent.	Lime method. Per cent.	Lindo-Gladding method. Per cent.
1'02	1'29	4'11	4'12
1'42	1'62	1'06	1'29
4'51	4'53	3'91	4'02
2'33	2'20	1'96	1'89
1'91	1'91	2'59	2'63
1'97	1'87	2'46	2'48
2'42	2'42	4'36	4'47
1'95	2'12	3'12	2'93
2'54	2'64	2'10	2'08
2'56	2'45	2'52	2'26
2'44	2'36	2'11	2'27
1'09	1'04	2'50	2'76
1'10	0'90	4'37	4'33
2'14	1'89	2'49	2'74
1'75	1'89	1'75	1'89
1'66	1'88	1'95	1'66
1'76	1'88	3'91	3'86
2'59	2'44	1'21	1'44
1'40	1'65	1'50	1'80
0'84	0'80	1'49	1'32
4'33	4'53	5'33	5'65
2'44	2'35	2'16	2'00
2'41	2'35	4'26	4'10
5'24	5'17	2'72	2'76
1'58	1'73	2'49	2'76
2'29	2'08	3'41	3'40
0'81	0'98	2'51	2'67
2'37	2'29	4'21	4'04
3'66	3'90	2'77	2'41
2'44	2'88	2'04	1'88

TABLE II.—*Determination of Potash in Fertilisers containing Organic Materials.*

(Samples treated with dilute sulphuric acid and incinerated prior to solution in water).

Lime method. Per cent.	Lindo-Gladding method. Per cent.	Lime method. Per cent.	Lindo-Gladding method. Per cent.
2'16	2'21	1'59	1'57
1'87	1'84	2'73	2'59
2'58	2'53	1'32	1'46
1'71	1'70	2'37	2'10
1'31	1'51	2'71	2'61
2'13	2'24	2'65	2'53
2'27	2'39	2'16	2'20
2'46	2'48	2'61	2'89
1'48	1'49	1'62	1'82
1'35	1'08	2'66	2'42
1'59	1'60	2'38	2'08
2'07	1'80	1'97	1'78
1'51	1'50	1'16	1'20
2'49	2'38	2'44	2'63
2'37	2'60	2'20	2'29
1'92	1'96	3'22	3'11
1'66	1'70	2'21	2'13
2'59	2'45	1'31	1'31
2'33	2'38	2'41	2'28
2'09	2'11	2'28	2'33
2'12	1'96	3'67	3'46
3'46	3'33	3'38	3'36
2'41	1'93	0'74	0'84
2'47	2'50	2'34	2'22
2'46	2'73	2'69	2'60
4'84	4'69	2'43	2'44
2'53	2'57		

TABLE III.—*Determination of Potash in Fertilisers containing Organic Materials.**Lime Method.*—Samples ignited before solution.*Lindo-Gladding Method.*—Unignited sample boiled with water.

Lime method. Per cent.	Lindo-Gladding method. Per cent.	Lime method. Per cent.	Lindo-Gladding method. Per cent.
1'62	1'66	4'00	3'87
2'02	2'19	0'50	0'60
2'14	2'11	2'18	2'47
0'88	0'74	1'18	1'20
1'11	1'06	1'96	1'73
1'82	1'55	1'78	1'68
1'53	1'68	2'00	2'07
1'61	1'63	2'09	2'35
3'09	3'02	1'52	1'62
1'84	2'06	1'80	1'78
2'05	2'10	2'17	2'25
2'43	2'32	1'62	1'70
2'52	2'65	1'65	1'71
2'95	2'86	2'38	2'43
2'00	2'29	1'83	1'64
1'95	2'03	2'63	2'37
1'92	2'11	2'88	2'60
2'58	2'74	2'24	2'21
2'38	2'23	2'97	2'94
1'92	2'09	1'43	1'26
2'71	2'64	1'95	2'06
1'56	1'34	1'84	2'14
1'98	1'96	1'93	2'14
1'15	1'28	2'37	2'56
2'28	2'54	1'65	1'81
1'29	1'53	3'70	3'46
2'53	2'29	3'41	3'52
1'32	1'28	1'54	1'30
2'26	2'07	1'35	1'48
1'50	1'49	2'68	2'80
1'88	1'60	2'85	3'13
2'94	3'00	3'03	3'02

TABLE IV.—*Determination of Potash in Fertilisers containing Organic Materials.*

(Samples boiled with water).

Lime method. Per cent.	Lindo-Gladding method. Per cent.	Lime method. Per cent.	Lindo-Gladding method. Per cent.
1'27	1'21	2'35	2'49
1'04	1'15	2'50	2'05
2'71	2'61	2'69	2'31
1'34	1'16	2'15	2'18
1'74	2'06	1'54	1'17
1'38	1'21	1'95	2'04
2'87	2'44	2'57	2'35
2'65	2'35	2'50	2'24
2'28	1'83	2'19	2'14
2'50	2'54	2'11	2'11
1'28	1'25	1'16	1'20
2'41	2'14	2'43	2'45
1'43	1'08	1'29	0'99
1'79	1'71	2'17	2'24
5'51	5'51	5'85	5'56
5'03	4'61	2'16	1'87
2'01	1'92	2'30	1'83
2'48	2'18	2'43	2'09
2'70	2'20	2'40	2'25
2'64	2'40	1'00	1'10
3'42	3'38	2'41	1'93
2'53	2'42	2'30	2'10
2'23	1'80		

The modification possesses several advantages over the Lindo-Gladding method:—(1) The precipitation of lime is

immediate, and there is no delay at this point; (2) evaporation to expel ammonia salts is eliminated; (3) probable

loss of potash during evaporation is obviated; (4) washing the potassium platonic chloride with alcohol and ammonium chloride "wash" may be performed thoroughly with greater ease and rapidity, while no larger amount of platinum is required than by the Lindo-Gladding method.

The accuracy of the method is evidenced by results, as shown in the tables. It has been used by the writer upon several hundred samples of miscellaneous fertilisers as a check against the Lindo-Gladding, and it is evident that the modification would not be applicable to fertilisers containing ammonia salts.

Table I. gives parallel results by the milk-of-lime and the Lindo-Gladding methods upon fertilisers containing no organic materials, solution in each case being made by boiling the sample with water.

Inspection of the tables reveals differences ranging from 0.01 to 0.27 per cent, with two exceptions, in a total of 60 samples. Of this number 46 show differences less than 0.20 per cent, while the average difference is 0.10 per cent.

This average difference is, of course, without value as an indication of accuracy, unless considered in connection with the variation of each parallel determination, but when so large a percentage of duplicates falls within the limits of probable error the average in differences of the entire number of determinations indicates in a measure the comparative accuracy of the two methods.

Considering that the figures in the tables represent first results, and in no case a second determination by the same method, results by the milk-of-lime method appear quite as reliable as those obtained by the Lindo-Gladding method. In the regular course of laboratory work, duplicate determinations by one and the same method may easily show less closely agreeing results.

Table II. shows parallel results obtained from fertilisers containing organic materials, the samples in each case being treated with dilute (1:1) sulphuric acid and incinerated before making solution in water.

By reference to Table II., we find variations ranging from 0.01 to 0.48 per cent in a total of 53 determinations. Forty-one of these give differences of 0.20 per cent or less, results averaging 0.06 per cent higher by the lime method than by the Lindo-Gladding.

Table III. contains results from fertilisers containing organic materials. Samples were ignited with sulphuric acid (1:1) before obtaining solutions for the lime method; while for the Lindo-Gladding, solution was obtained by boiling the unignited sample with water.

These results show an extreme variation of 0.29 per cent in a total of 63 determinations. Forty-six of the 63 vary less than 0.20 per cent, while the results average 0.02 per cent lower by the lime method.

In Table IV. may be found results on fertilisers containing organic materials, solutions of both methods being obtained by boiling the sample with water. The solutions for the lime method were considerably coloured by dissolved organic matter.

Although little was expected from the results obtained by the lime method under these conditions, still they show an extreme variation of only 0.55 per cent in a total of 45 determinations, while 30 of the 45 differ less than 0.30 per cent, and the average difference is only 0.15 per cent. Nothing is claimed for the method when used under these conditions, but it is interesting to note that the method gives many good results, even when precipitation of platinum takes place in a solution considerably coloured with organic matter.

Analysis of Steel Works Material.—M. Beranger has made arrangements with Messrs. Longmans, Green, and Co. for the issue of a French translation of Brearley and Ibbotson's "Analysis of Steel Works Materials."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, December 3rd, 1903.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. M. Kemp-Welch and J. T. Ainslie Walker were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Denys Cowper, 3, Bishop's Mansions, Fulham, S.W.; Nevil Norton Evans, McGill University, Montreal, Canada; John Monteath Guthrie, 199, Ferry Road, Leith, N.B.

The PRESIDENT announced that since the last meeting a photograph of the portrait of Roger Bacon, which is in Knoke House, had been presented to the Society by Mr. Oscar Guttman.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Robert Duncombe Abell, Ph.D., D.Sc.; Percy Appleyard; Edward F. Armstrong, Ph.D.; Herbert Henry Ashdown; Herbert Moore Attwell; William Cornish Badcock, B.A.; Harold James Bailey; Thomas Vipond Barker; Harold Goodenough Bayly; Charles Marsh Beadnell; William Beam, M.A., M.D.; Henry James Wheeler Bliss; Nicholas John Bluman; Paul Brühl; Erasmus Robert Buggé; William Clacher; William Thomas Deeks; Ernest Derwent; Henry Russel Ellis; Charles E. Fawsitt, Ph.D., B.Sc.; William Forster; John Albert N. Friend, M.Sc.; Ernest A. Gardiner, B.A.; Frank Brooks Gatehouse; Percy William Gent; Frank Barnes Grundy; John T. Hall; Harold Montague Heasman; Arthur V. Hendrickson; John George Howarth; Edwin Reginald Hughes; Herbert Hymans; Edward Charles Ibbotson; William Henry Jackson; Walter Ernest Jennings; Thomas Oliver Kent; John J. Kielty; Thein Kin, B.A.; Harley Fancutt Knight; John Laing; Francis E. E. Lamplough, B.A.; Henry William Lawrence; Harold Duff Leadbetter; Gervaise Le Bas, B.Sc.; David Baird Macdonald; Frederick William McMahon; Ernest William Mann; Gordon W. Monier-Williams, B.A.; Urban Orlando S. Nairne; James Victor Nevill; William Parry, B.Sc.; Henry George Pike; George Horace G. Plymen; William Branch Pollard, B.A.; Mata Prasad, M.A.; Herbert Stanley Redfern, B.Sc.; Stiles William George Rich; Harold E. Richardson, B.A., B.Sc.; Philip Wilfred Robertson; William David Rogers; George Senter, Ph.D., B.Sc.; Arthur Slator, Ph.D., M.Sc.; Frank Gurney Smith; William Veysey Smith, B.A.; Alfred Walter Stewart, B.Sc.; Arthur Tighe; Arnold Turner; William Ernest S. Turner, B.Sc.; Miles Walker-Pole; Carl Friedrich R. Weiss, Ph.D.; Fred Wright.

Of the following papers those marked * were read:—

*158. "The Molecular Formula of some Fused Salts as Determined by their Molecular Surface Energy." By J. F. BOTTOMLEY.

The electrolytic conductivity of fused salts has not been satisfactorily explained, but it might be expected that ionisation would be produced by the presence of complex molecules, and, at Sir William Ramsay's suggestion, measurements of the variation of the capillary rise with temperature were undertaken with the object of testing this point. The determinations with lithium and silver nitrates, potassium chlorate and dichromate, zinc and stannous chlorides were unsatisfactory owing to experimental difficulties, and successful results were obtained only with sodium and potassium nitrates. The average value of K for sodium nitrate is 0.503, and for potassium nitrate 0.445, instead of 2.12, the normal value for non-associating substances. This implies that 9 or 10 molecules of the simple salt, NaNO_3 or KNO_3 , are associated to form a complex, the supposition that a portion of the salt is ionised by the complex molecules of another portion being therefore rendered probable.

*159. "The Atmospheric Corrosion of Zinc." By G. T. MOODY.

The recorded observation that hydrogen peroxide may be detected during the oxidation of zinc in presence of water has been brought forward by Dunstan in support of his contention that, in the case of iron, hydrogen peroxide "is a necessary intermediate product of the chemical change involved in rusting" ("Report of the Steel Rails Committee of the Board of Trade, 1900; *Proc.*, xix., p. 152). It consequently appeared of interest to determine if the scale formed during the atmospheric corrosion of zinc showed a composition which would justify the assumption that it is to be regarded as an oxidation product formed by the interaction of metal, water, and oxygen. To this end, strips of thin sheet zinc were suspended in a muslin bag under the shelter of a north wall, and exposed to the full effects of the atmosphere for five months. At the end of this period, the semi-crystalline scale was detached from the metal and dried; it had a composition closely agreeing with the formula $\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$. The production of this basic carbonate may be regarded as evidence that the atmospheric corrosion of zinc is to be attributed not to direct oxidation of metal, but to an interaction with carbonic acid. This view is supported by the behaviour of zinc in a saturated solution of carbon dioxide. The metal dissolves with evolution of hydrogen and formation of zinc hydrogen carbonate. The resulting solution, when heated or exposed to air, becomes turbid, and on spontaneous evaporation yields a basic carbonate agreeing in composition with the product of atmospheric corrosion.

Whilst zinc is rapidly converted into hydroxide by commercial hydrogen peroxide, this metal, like iron, remains practically unattacked when in contact with pure 30 per cent peroxide. The statement made by Dunstan (*loc. cit.*) that iron, zinc, and lead behave similarly towards hydrogen peroxide, is not in agreement with the observations of the author, who finds that the addition of a few m.grms. of assay lead induces immediate decomposition of 30 per cent peroxide, oxygen and steam escaping with almost explosive violence. The lead becomes superficially coated with brown peroxide, and presents an appearance quite different to that arising from atmospheric corrosion.

The author concludes that the atmospheric corrosion of zinc, like that of iron, is the result of interaction between metal and acid, and that the attack on zinc is less marked because the acid is in a great measure retained in combination as basic carbonate.

*160. "The Formation of Urea by the Direct Hydrolysis of Lead Cyanate." By A. C. CUMMING.

Lead cyanate is readily and quantitatively transformed into lead carbonate and urea by direct hydrolysis with boiling water: $\text{Pb}(\text{CNO})_2 + 2\text{H}_2\text{O} = \text{PbCO}_3 + \text{CON}_2\text{H}_4$. This salt, which is prepared by adding lead nitrate to potassium cyanate solution from which the carbonate has previously been removed by barium nitrate, is fairly stable at the ordinary temperature, and may be washed with cold water until free from impurities.

The progress of the change was followed qualitatively with a polarising microscope, advantage being taken of the fact that the small acicular crystals of lead cyanate which polarise light are gradually replaced by amorphous granules of lead carbonate.

The action was also followed quantitatively by a titration method which depends on the fact that lead cyanate neutralises twice as much acid as the products of its hydrolysis.

No evidence was obtained of the formation of ammonium cyanate, and this method is therefore distinct from any earlier synthesis.

DISCUSSION.

The PRESIDENT expressed surprise that this reaction had not already been observed, remembering the use of lead cyanate in a process introduced many years ago by the late Mr. John Williams for the manufacture of urea (*Journ. Chem. Soc.*, 1868, xxi., 63).

161. "Acid Salts of Monobasic Acids." By R. C. FARMER.

The substituted benzoic acids have the general property of forming salts containing one molecule of the free acid to one molecule of neutral salt. The potassium and ammonium salts were taken as typical, and the acid salts of benzoic acid and its methyl-, hydroxy-, bromo-, and nitro-derivatives were examined. These substances form well-defined, crystalline compounds, which do not undergo any change at the melting-points of the free acids; they are not affected by inert solvents, but are at once decomposed by water. Experiments on the ratio of distribution of the acids between benzene and aqueous solutions of their normal salts showed that these acid salts do not exist to any appreciable extent in aqueous solution. In alcohol, on the other hand, the dissociation is only partial, as was shown by molecular weight determinations at the boiling-point.

162. "The Solubility Curves of the Hydrates of Nickel Sulphate." By B. D. STEELE and F. M. G. JOHNSON.

The solubilities of the hydrates of nickel sulphate have been determined at temperatures ranging from -5° to 99° , and equilibrium curves have been constructed for the following hydrates: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue quadratric), and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green monoclinic). A fourth hydrate is deposited from saturated solutions at temperatures above 118° , and the salt separating at 131° has been analysed and found to be the dihydrate, $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$.

The following quadruple-points have been fixed:—1. The cryohydrate-point of the heptahydrate (-4.15°). 2. The transition-point (31.5°): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue) + saturated solution. 3. The transition-point (53.3°): $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue quadratric) $\rightleftharpoons$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green monoclinic). The transition-point of the change: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ + saturated solution, has not been determined.

163. "Action of Malt Diastase on Potato Starch Paste." By B. F. DAVIS and A. R. LING.

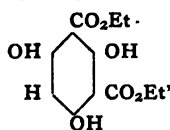
In continuing their earlier experiments (*Journ. Fed. Inst. Brewing*, 1902, viii., 475), the authors show that a solution of diastase, when heated above 55° , becomes weaker in its action, and that the alteration produced in the enzyme molecule is a permanent one, for the diastase retains its acquired properties when it is reprecipitated from its solution by alcohol, and allowed to act on starch paste at or below 55° . The altered diastase produces *d*-glucose when it acts on starch paste, and the change appears to commence when a solution of the enzyme is heated below 60° , although, judging from the small amount of *d*-glucose produced, the reaction is not complete at this temperature. As the temperature of the initial heating is raised, the amount of *d*-glucose produced by the enzyme also increases, the maximum amount being obtained by the action of diastase, which has been previously heated in solution at 68 – 70° for fifteen to thirty minutes. Above this temperature, the destruction of the enzyme is so rapid that a much larger proportion has to be employed to attain that stage of the reaction at which *d*-glucose appears. Nevertheless, *d*-glucose is formed by diastase which has been heated to 78° , and probably at even higher temperatures. It has been observed in all cases that when the solution is kept at the temperature of hydrolysis (usually 55°) after the maximum amount of *d*-glucose has been formed, the amount of this sugar present diminishes, and the occurrence of this apparent condensing action of the enzyme may probably in several cases explain the failure to detect *d*-glucose among the products of hydrolysis. The maximum amount of *d*-glucose formed in any case does not exceed about 12 per cent of the total hydrolytic products.

164. "The Formation of Phloroglucinol by the Interaction of Ethyl Malonate with its Sodium Derivative." By C. W. MOORE.

In the year 1885, Baeyer made the important discovery that when ethyl malonate is heated with its sodium derivative at 145° , a derivative of phloroglucinol is formed,

which melts at 104° , and which Baeyer considered was ethyl phloroglucinoldicarboxylate, $C_6(OH)_3(CO_2Et)_3$ (*Ber.*, 1885, xviii., 3457).

During the course of an investigation involving the use of ethyl malonate, the author was led to re-investigate this matter, and he has been able to prove that the substance formed under the conditions employed by Baeyer is ethyl phloroglucinoldicarboxylate, $C_6H(OH)_3(CO_2Et)_2$, and not the above-mentioned tricarboxylate. The molecular weight determination in benzene solution gave 273 and 270, whereas the molecular weights of the dicarboxylic and tricarboxylic esters are 270 and 342 respectively. The determination of the ethoxyl groups, which was carried out by Dr. W. H. Perkin, sen., also gave numbers which clearly show that the substance is a dicarboxylic ester. When treated with bromine, it yields a bromide having the composition $C_6Br(OH)_3(CO_2Et)_2$, which was first prepared by Bally (*Ber.*, 1888, xxi., 1770). Since it also yields a triacetyl compound when heated with acetic anhydride, there can scarcely be a doubt that Baeyer's ester must be represented by the formula—



and that it is therefore ethyl phloroglucinoldicarboxylate.

PHYSICAL SOCIETY.

Ordinary Meeting, December 11, 1903.

Mr. JAMES SWINBURNE, Vice-President, in the Chair.

A PAPER ON "A Method of Mechanically Reinforcing Sounds" was read by the Rev. T. C. PORTER.

If a tuning-fork be sounded and placed in a flame, there is a very marked reinforcement of the sound. This is proved not to be due to resonance in the ordinary sense, but to the change from continuous to intermittent combustion. Under certain circumstances the impulses given to the air external to the flame, by the waves of burning gas, are more forcible than those given by the unaided sounding body. Thus a new way of reinforcing the sounds given by a vibrating body is found; and the rest of the paper demonstrates this for the phonograph, a flame being used instead of the ordinary trumpet. Coal-gas and air are brought by tubes into the chamber of the "reproducer," and thence to a jet, where they are burnt. The vibrations of the reproducer are thus impressed on the issuing gas and air, which burn synchronously with them, the sounds thus emitted being easily heard over a large room. In practice it is found best to spread out the flame by a second jet of air, or of mixed air and gas, placed close to the first jet and at right angles to it. The author describes the nature and quality of the sounds emitted by the flame, and the modifications of these which may be produced. If the first jet is used alone, and a common blowpipe-flame obtained from it, it is found that the sound is markedly reinforced by introducing a thin sheet of platinum foil near the blue tip of the inner cone. This reinforcement is attributed to the rapid expansion and contraction of the platinum in response to the variation in the heat of the flame caused by the sound-waves from the phonograph, and not to simple reflection of these waves from the platinum surface.

The CHAIRMAN read a letter from Mr. Chichester A. Bell expressing his interest in the subject of Mr. Porter's paper, and pointing out that the whole matter had been described by him at length in a paper on "The Sympathetic Vibrations of Jets" (*Phil. Trans.*, 1886).

Mr. W. DUDDLELL suggested that the flame was in a condition of instability, so that any disturbance created in it tended to increase in amplitude. If the energy for the increased sound came from the tuning-fork, and the flame

simply acted as a trumpet, then the forked would be rapidly damped; but if the flame was unstable the tuning-fork would not be rapidly damped. He asked the author if he had tried experiments on this point.

Prof. A. S. HERSCHEL referred to the ways in which energy could be transmitted by a gas (1) by a flow and (2) by the passage of undulations. The second method was concerned in the experiments shown by the author. In reply to a question by Prof. Ayrton he said he did not think that the increased sound was due to an increase in the amplitude of vibration of the tuning-fork.

Mr. D. J. BLAILEY asked if the flame could be so adjusted as to restore a wave-form having a complicated distribution of upper partials, or whether it could only reinforce pure tones. (The CHAIRMAN pointed out that in the experiments shown with the phonograph the distinctive character of the notes emitted by the various instruments could be easily recognised).

Prof. H. L. CALLENDAR referred to Prof. Dixon's experiments on the propagation of explosive waves through gases. These waves had been photographed, and proved that the passage of a detonation-wave through an explosive mixture caused a local heating, shown by a corresponding brilliance in the photograph. Complicated effects were produced by the meeting of a detonation- and a detonation-wave, but in every case there was an increase of chemical action in the flame. He suggested that the behaviour of the platinum foil in the blowpipe jet might be ascribed to the meeting of two such waves.

Mr. PORTER, replying to Mr. Duddell, said a tuning-fork was unquestionably rapidly damped when placed in a flame. With regard to Prof. Callendar's observations, he said he had looked in vain for anything corresponding to the existence of loops or nodes in the flame. Referring to Mr. Blaikley's remarks, he said that a small flame reinforced the high notes better than the lower ones, and *vice versa*.

A paper on "The Simmance-Abady 'Flicker' Photometer" by Messrs. SIMMANCE and ABADY was read by Mr. SIMMANCE.

The principle of the flicker photometer, discovered by Prof. O. N. Rood ten years ago, has frequently been remarked on, but attempts to design a reliable apparatus depending upon this principle have hitherto been unsuccessful. The authors, guided by the following rules, have designed a photometer which is capable of balancing and comparing the most violently contrasted tints:—The light effects must be in juxtaposition without any apparent division line, and must move, oscillate, or rotate so that the point of juncture of the rays of the two lights passes and returns entirely across the vision-field. Any hiatus, or longer exhibition of one light than the other, biases the result. The observation surfaces, or surfaces upon which the light rays fall, must be at exactly the same distance from the eye, at exactly the same angle in relation to the line of sight, and must be of pure white, such as is afforded, for example, by a clean chalk, plaster-of-Paris, magnesium carbonate, or barium sulphate; any tint affects the accuracy of the result. The observation surfaces must also themselves in turn occupy the field of vision; an apparent movement or optical illusion does not afford accurate results.

Observations made with the photometer, by operators suffering from colour-blindness, astigmatism, &c., make it certain that the relative intensities of two lights, whether of the same colour or different, can be accurately and easily gauged by the method. The authors submit that the Purkinje phenomenon does not affect the accurate working of the instrument, as it is a purely colour effect, and colour does not enter into consideration in this photometer. The photometer itself consists of a wheel of a white material with a specially shaped periphery, which wheel is caused to revolve before an eyepiece by means of a suitable motor. At right angles to the line of sight, and parallel with the axis of the revolving wheel, are the two lights undergoing examination, the rays of which fall upon the shaped periphery of

the wheel, enabling the effect of each light to be seen in turn through the eyepiece.

Prof. W. E. AYRTON said it was an important question to settle exactly what the photometer measured. The fact that different observers using the same photometer obtained the same results for the ratio between two lights did not prove that the instrument actually compared intensities. He had come to the conclusion that when the distances between the sources of light and the photometer were great the results were not affected by the Purkinje effect.

The Rev. T. C. PORTER expressed his interest in the instrument, and said there was no doubt that the flicker photometer measured intensity independent of colour. The results obtained directly from a flicker photometer agreed with those deduced by indirect methods from observations with ordinary instruments.

Mr. L. GASTER expressed his admiration for the photometer, and explained that this type of instrument was becoming more important because of the great number of improvements made during the last few years in the manufacture of incandescent lamps and arc-light carbons by the addition of other substances to the pure carbon. A great step towards the simplification of the process of photometry had been attained by Prof. C. P. Mathews, by the aid of whose photometer one is enabled to get in one reading an illumination upon the screen, proportional to the mean spherical intensity of the source.

Dr. W. WATSON said the authors had compared a red light with a white light, and also a blue light with a white light. He asked if they had compared a red with a blue directly, and if so, how the results agreed with those deduced from the comparison of both with a white light.

Mr. W. DUDELL asked what was meant by the equality of two lights of different colours. Was it judged by the eye, the bolometer, or the flicker effect? On account of the Purkinje effect the inverse square law could not be used, and he asked for the real fundamental relation underlying the use of the instrument.

Mr. J. ABADY, replying on behalf of the authors, said the discussion had turned mainly on two points:—(1) Does the instrument measure candle-power? and (2) is it independent of the Purkinje effect? If a Bunsen disc were taken and used to compare the candle-powers of two lights of the same colour, the grease-spot vanished at a certain point. If a flicker photometer was substituted for the Bunsen disc, the flicker disappeared at the same point. In both cases candle-power had been measured. In reply to Prof. Ayrton he said that results obtained from the photometer by different observers agreed among themselves and also agreed with results obtained from the Bunsen disc photometer. With regard to the Purkinje effect, he did not think it affected the readings of a flicker photometer, because the same values for the ratio between the intensities of two different coloured lights were obtained by varying the distances of the lights from the instrument within wide limits. Answering Dr. Watson, they had carried out the experiments suggested, and the results from the direct and the indirect comparison were in absolute agreement.

Mr. ROLLO APPELBYARD exhibited a Conductometer, the theory and mechanical details of which are fully described in the *Proceedings of the Institution of Civil Engineers*, vol. cliv., Session 1902-3, Part IV.

Prof. L. R. WILBERFORCE exhibited a Model to illustrate various Properties of Wave-motion.

The model consists of a series of brass balls suspended in a line by spiral springs and capable of transverse or up and down motion. The balls can be set in vibration by releasing them from extreme positions by means of triggers, one set of triggers controlling the up and down motion, and another set the pendular. If the vertical and transverse periods are unequal, the release of the triggers in rapid succession produces a disturbance similar to that produced by the passage of light through a crystal. If

the periods are nearly equal effects are shown similar to those observed with Lissajous figures. If the balls are joined together by horizontal springs, condensations and rarefactions can be exhibited. If two of the balls near one end are constrained to move up and down only, and two near the other end are constrained to move transversely, the phenomenon of polarisation can be illustrated. If the balls are put in neutral equilibrium, by supporting them on the upper ends of vertical rods, when suspended by spiral springs which very nearly balance their weights, the reflection of both transverse and longitudinal waves at surfaces of infinite and zero density can be illustrated. By substituting, for some of the vertical rods, vertical rectangular frameworks with heavy pendulum-bobs hanging from the upper sides, the phenomenon of anomalous dispersion can be exhibited.

NOTICES OF BOOKS

Liquid Fuel and its Combustion. By WM. H. BOOTH.
Westminster: Archibald Constable and Co., Ltd. 1903.

THE first part of this book deals with the theory and principles of the subject, and the second with their application to practice. This latter part describes in detail the various systems adopted in using liquid fuel at sea, for stationary purposes and for locomotives; the Holden system as used by the Great Eastern Railway naturally occupies an important place, but those employed in other countries are not by any means neglected. The analysis of flue gas is discussed in a chapter which has been revised by Mr. Horace Allen. The author in the preface has forestalled the obvious criticism regarding the omission of the consideration of some aspects of the subject which might have been expected to be found in such a treatise, and possibly the requirements of readers will justify his selection in most cases; the practical impossibility of including in one volume the description of all methods of utilising liquid fuel will explain the selection of types only of apparatus. The earlier part on the theory and principles is less satisfactory. Some elementary details, which, moreover, hardly seem to have much bearing on the subject, are treated in a misleading manner, as in the pages dealing with heat and temperature, and nowadays it can no longer be stated as an axiom that the scientific man rejoices at the inutilty of the discovery he has made. Judging by this specimen of what results when those to whom science is "less familiar, but more attractive," step into the breach caused by the neglect of important industrial methods by scientific men, their efforts are not likely to be attended with enough of success to make it appear advisable to recommend the practice to others in the same category.

Manuel Guide de la Fabrication du Sucre. ("A Manual on the Manufacture of Sugar"). By R. TEYSSIER.
Paris: C. Naud. 1903.

THIS handbook does not aspire to be a complete treatise on the manufacture of sugar, but aims at describing in as simple language as possible the ordinary appliances to be found in a factory, with the methods of using them, and the means generally adopted to obviate difficulties and remedy accidents. The chemistry of the process receives only very meagre attention, and the book will be found more useful by foremen and works managers than by chemists. The advice and hints given are all thoroughly practical, and the author has evidently had considerable experience in the management both of workmen and machinery. A great deal of the matter, however, would seem to be better and more easily learnt in the factory itself than from the best text-book ever written, though, on the other hand, a good many useful suggestions might be gathered from the pages which deal with the building of an ideal sugar plant

and its management. An appendix of very elementary mathematical results seems somewhat out of place in such a book, but the other tables are very full, and will be constantly found useful for reference.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. Band IV. 9-11 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1903.

THE first article of this issue deals with the important question of the conditions of action of the fibrin ferment and its bearing on the coagulation of the blood. The author, Dr. P. Morawitz, adopts Alexander Schmidt's views, and endeavours to explain the discrepancies between them and those of later investigators; but he cannot be said to have done very much towards the elucidation of this obscure problem, though he has apparently subjected it to a careful investigation. Another interesting paper, by Dr. Otto von Fürth, describes researches on the behaviour of the oil in seeds during germination; in the course of the experiments it was hoped that some light would be thrown on the transformations which fat undergoes in the animal body. Although this hope was not realised the results of the experiments, which were carried out with the seeds of helianthus and ricinus, are very interesting. Most of the other papers are mainly concerned with physiological questions, and are not of much interest to the chemist.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 20, November 16, 1903.

New Preparation of Argon.—H. Moissan and A. Rigaut.—The authors have already proved that the metal calcium combines easily with nitrogen at a dull red heat, giving a crystalline nitride of formula Ca_3N_2 . As metallic calcium possesses also the property of fixing hydrogen at the same temperature, giving a crystalline hydride of formula CaH_2 , and this hydride does not dissociate at 500° , they now apply these different properties of calcium for the extraction of argon from the atmosphere. The process consists of four operations:—(1) The preparation of 100 litres of nitrogen; (2) the gradual enrichment of the argon in the nitrogen; (3) The first purification; (4) a second purification of the argon by circulation over calcium.

Exact Separation of certain of the Rare Earths.—G. Urbain and H. Lacombe.—(See p. 295).

Acetylenic Acetones. New Method of Synthesis of the Isoxazols.—Ch. Moureu and M. Brachin.—The authors have previously established the fact that the acetones with acetylenic function $\text{R}-\text{C}\equiv\text{C}-\text{CO}-\text{R}'$ give, on reaction with the hydrazins, pyrazols identical with those from which the β -diketones are derived on hydration. They now investigate the action of hydroxylamine on the same compounds, and find that isoxazols are obtained, the yield being quantitative.

Retrogradation of Amidon Starch.—L. Maquenne.—In a preceding research the author showed that amidon starch retrogrades with time; that is to say, becomes in part insoluble. This transformation is subordinate to a large number of independent variables, such as temperature, the nature of the medium, concentration, &c. He now investigates the influence of temperature and of the mineral acids employed in sufficient quantity to start saccharification. He finds—(1) That retrogradation is

more rapid and complete as the temperature is lower; (2) the phenomenon is assisted by the presence of mineral acids, even in so small a proportion as $1/10,000$; (3) it tends towards a limit, which in a neutral medium at 0° appears to be about 30 per cent.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—

A Christmas Course of Lectures (illustrated by lantern slides and adapted to a juvenile auditory) on "Extinct Animals," by Professor Ray Lankester. To be delivered on the following days at 3 o'clock:—Tuesday, Dec. 29, Thursday, Dec. 31, 1903, and Saturday, Jan. 2, Tuesday, Jan. 5, Thursday, Jan. 7, Saturday, Jan. 9, 1904.

Professor L. C. Miall, Fullerian Professor of Physiology, R.I., six lectures on "The Development and Transformations of Animals."

Mr. E. Foxwell, three lectures on "Japanese Life and Character."

Dr. E. A. Wallis Budge, two lectures on "The Doctrine of Heaven and Hell in Ancient Egypt" and "The Books of the Underworld."

Mr. G. R. M. Murray, three lectures on "The Flora of the Ocean."

Mr. A. D. Hall, three lectures on "Recent Research in Agriculture."

Professor H. L. Callendar, three lectures on "Electrical Methods of Measuring Temperature."

Mr. Sidney Lee, two lectures on "Shakespeare as Contemporaries knew him."

Mr. J. A. Fuller-Maitland, three lectures on "British Folk-Song" (with vocal illustrations).

Mr. W. L. Courtney, two lectures on "Comedy—Ancient and Modern."

The Right Hon. Lord Rayleigh, six lectures on "Physics."

During the Season 1904 the lectures on Tuesdays and Thursdays will be delivered at 5 o'clock, and the Saturday lectures at 3 o'clock.

The Friday Evening Meetings will begin on January 15, when a Discourse will be delivered by the Right Hon. Lord Rayleigh on "Shadows." Succeeding Discourses will probably be given by the Rev. Walter Sidgreaves, Mr. D. G. Hogarth, Mr. Alfred Austin, the Dean of Westminster, Mr. H. Brereton Baker, Mr. Alexander Siemens, Professor W. Stirling, Professor F. T. Trouton, Mr. Henry Arthur Jones, Professor Dewar, and other gentlemen.

The Electrolytic Preparation of Free Periodic Acid.—E. Muller and O. Friedberger.—The authors electrolysed a solution of iodic acid with an anode covered with PbO_2 . To estimate the HIO_4 formed, in the presence of the remaining HIO_3 , they neutralised with soda until phthalein took a rose colour, added CO_2NaH and KI, then with a titrated solution of As_2O_3 they estimated the iodine set at liberty; the weight of oxygen fixed by the As_2O_3 is a quarter of that contained by the HIO_4 . As for the total oxygen of the iodic and periodic acids, it is estimated by means of $\text{S}_2\text{O}_3\text{Na}_2$ in solution acidulated with sulphuric acid and treated with potassic iodide. The preparation of HIO_4 is effected in a small cell in which the porous pot contains the solution of HIO_3 at 50 per cent, and an anode formed of a lead tube, traversed by a stream of cold water if necessary, and having its surface covered with a layer of electrolytic PbO_2 . The outer vessel contains a bi-normal solution of sulphuric acid, and a cathode consisting of two sheets of platinum. The details of the experiments will be found in the original paper; in one of them, after four and a-half hours electrolysis with a current of 2 ampères and 6 volts, equal to a density of current of 28 ampères per square c.m., the oxidation was complete. The solution in the porous pot is slightly brown, and

cloudy in appearance; it is diluted considerably, filtered, and concentrated on the water-bath; on cooling it then gives large crystals of HIO_4 containing a little sulphuric acid; these can be purified by draining and re-crystallisation. Bromic acid does not give BrO_4H under the same conditions.—*Berichte*, vol. xxxv., p. 2652,

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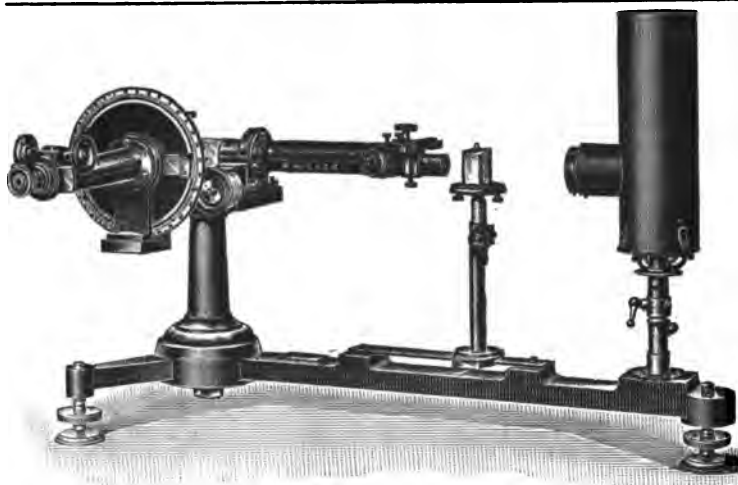
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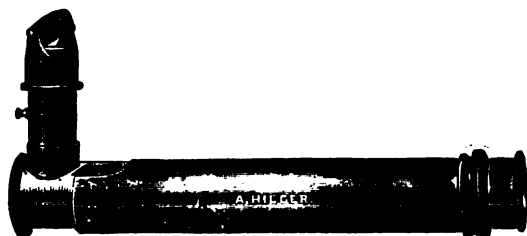
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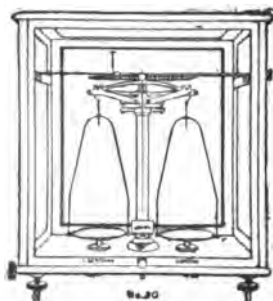
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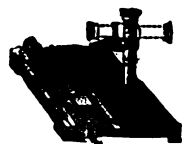
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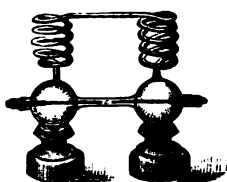
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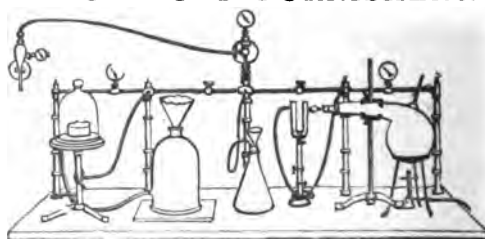
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THE CHEMICAL NEWS.

VOL. LXXXVIII., No. 2300.

FLUORIDE OF GOLD.*

By VICTOR LENHER.

INASMUCH as fluor spar is frequently associated with gold in nature, and quite notably so in the deposits of the telluride ores, it has seemed important to study gold fluoride in order to determine, if possible, whether this substance can play any part in the genesis of these deposits.

The known compounds of gold with the halogens chlorine, bromine, and iodine, are, as a rule, fairly well defined. In the trivalent condition, gold forms the relatively stable chloride, while the bromide and iodide show greater tendency to break down into the lower state of valence of gold.

The halides in which gold shows a monovalence have received considerable attention, and it is known with a reasonable degree of certainty under what conditions aurous chloride, bromide, and iodide are capable of existence.

While the chlorides, bromides, and iodides of gold have received more or less study, comparatively little is known of fluoride of gold. Prat (*Comptes Rendus*, lxx., 843) has prepared an intermediate oxide of gold, Au_2O_2 by the incomplete solution of gold in aqua regia, in which the hydrochloric acid is in excess, treating the solution with sufficient potassium bicarbonate to dissolve the precipitate formed, and warming the clear orange-yellow solution to 95° , when a dark olive-green precipitate was obtained which, when dried, showed the composition Au_2O_2 . In studying the properties of this oxide, Prat states that hydrofluoric acid combines with it but without dissolving it. In his study of the action of fluorine on the various metals, Moissan states that at a red heat, gold is attacked by fluorine gas, a yellow hygroscopic substance being formed, and that this substance is readily decomposed into gold and fluorine.

These two experiments give practically what is known of the fluoride of gold.

The activity of the halogens toward other elements is, as a rule, inversely proportional to their atomic weights. The first member of this group of active elements, fluorine, is certainly the most active of all the elements, be they halogens or not; yet, as will be demonstrated later, it appears to have little if any affinity for gold.

In studying the chemistry of gold, it should always be borne in mind that it is the most inactive of the metals, but the relative stability of the most of its salts, notably with the halogens, would appear to make probable the relative stability of the compound of the most active of the elements, fluorine. On the other hand, we have the marked difference of fluorine from the other halogens in the insoluble fluorides of calcium, strontium, and barium, as contrasted with the very soluble chlorides, bromides, and iodides; and the soluble fluorides of silver and thallium as compared with the insoluble chlorides, bromides, and iodides.

In order to study the relations between fluorine and gold, experiments were conducted with the view of bringing about, if possible, the formation of gold fluoride under various possible conditions.

The first experiment made was a study of the action of hydrofluoric acid on gold oxide. To this end, gold oxide was prepared by the action of magnesium oxide on a solution of gold chloride, and the excess of magnesia removed with nitric acid. The gold oxide thus obtained was finely

divided, and hence in the most suitable condition to be susceptible to any chemical action. This gold oxide can remain in contact with hydrofluoric acid indefinitely, or, as has been the case, can be boiled for weeks with either hydrofluoric acid alone, or with a mixture of hydrofluoric and nitric acids, without suffering any change whatever. These experiments have been repeated several times, but in no case has gold been found to enter into solution, nor has it been possible to detect fluorine in the precipitate. It is obvious that gold fluoride cannot be prepared by the action of hydrofluoric acid on the oxide. The next most natural method to try for the preparation of the fluoride would be that of double decomposition.

Silver fluoride and gold chloride, both being soluble salts, on being brought in contact in solution should yield theoretically $AuCl_3 + 3AgF = AuF_3 + 3AgCl$. The actual case is that when solutions of these two salts are brought in contact, gold hydroxide is quantitatively thrown out of solution along with silver chloride; thus, $AuCl_3 + 3AgF + 3H_2O = 3AgCl + Au(OH)_3 + 3HF$. The accuracy of this reaction has been carefully established in the laboratory.

If gold fluoride is even momentarily formed, it is immediately decomposed by water.

The method yet remaining for the preparation of a substance incapable of existence in presence of water would be the use of anhydrous solvents. A large number of organic solvents have been tried with this end in view, but no substance has been found which would dissolve both gold chloride and silver fluoride; either these salts are insoluble or are decomposed by the substances worked with. Among the solvents examined, mention may be made of the following:—Alcohol, ether, carbon bisulphide, benzene, turpentine, pentane, hexane, chloroform, carbon tetrachloride, ethyl nitrate, nitrobenzene, ethyl acetate, ethyl propionate, and pyridine.

It thus appears that gold fluoride is incapable of existence not only in presence of water, but under the ordinary conditions met with in the laboratory and in nature.

A PROBABLE CAUSE OF THE DIFFERENT COLOURS OF IODINE SOLUTIONS.

By ARTHUR LACHMAN.

It is a well known fact that solutions of free iodine have different colours, depending in some way upon the nature of the solvent. Gautier and Charpy (*Comptes Rendus*, 1890, cx., 189; cxi., 645), who investigated this problem about twelve years ago, distinguished four sets of colours, of the following types:—

(1) Violet, e.g., chloroform; (2) red, e.g., ethylene bromide; (3) red-brown, e.g., toluene; (4) brown, e.g., alcohol.

A large number of solvents were thus classified, but the authors confessed themselves unable to find any relations between the chemical function of the solvent and the colour. The following year, Rigollot (*Comptes Rendus*, 1891, cxii., 38) determined the absorbing power of different iodine solutions for definite light waves; but his results led to no explanation. A few years later, an elaborate study of the problem was undertaken by Krüss and Thiele (*Zeit. Anorg. Chem.*, 1894, vii., 25). They ascertained the molecular weight of iodine in various solvents, and found that practically in all cases, where moderately dilute solutions were taken, the iodine molecule consists of 2 atoms. Variations from this value were irregular, both for brown and for violet solutions. Concentrated solutions usually gave high molecular weights, indicating association, but no change of colour accompanied this association.

In spite of these results, Krüss and Thiele attempt to explain the different colours by an assumption of different molecular weights: violet solutions containing I_2 , brown

* Read before the Wisconsin Academy of Science, December 26, 1902, and published in the *Transactions*. From the *Journal of the American Chemical Society*, xlv., No. 11.

solutions (I_2)_n, n being greater than 1. These complicated molecules, however, are supposed to give a normal molecular weight by all osmotic methods. This explanation is equivalent to saying that in brown solutions the molecular weight of iodine is much greater than in violet, but that none of our present methods are able to demonstrate the increase; and it involves a conception of the molecular theory whose utility yet remains to be shown. The change from brown into violet is ascribed to dissociation; if the above theory is correct, solvents with brown colour should have less dissociating power than those with violet. But this is contradicted by well-established facts; alcohol has much greater dissociating power than chloroform or benzene.

Notwithstanding the negative results of Gautier and Charpy, and of Krüss and Thiele, a simple causal connection seems to exist between the chemical behaviour of the solvent and the colour of iodine solutions. This relationship was not apparent to the above investigators *because in critical cases they observed wrong colours*, owing to impurities in the solvents. From the table given below, it will be seen that iodine solutions, when made with pure solvents have but two colours—violet and brown—with but one exception, which will be discussed below.

COLOUR OF IODINE IN VARIOUS SOLUTIONS.

A. Violet Solutions.

Hydrocarbons :—

Hexane.
Benzene (thiophene free).
Toluene (a).
o-Xylene (b).
m-Xylene.
p-Xylene.

Halogen compounds :—

Chloroform.
Ethylene chloride (c).
Ethylidene chloride.
Tetrachlorethylene (d).
Carbon tetrachloride.
Isobutyl chloride (e).
Amyl chloride.
Chlorobenzene.
Benzalchloride.
Benzotrlichloride.

Bromoform
Ethylene bromide (e, f).
Trimethylene bromide.
Amyl bromide (e).
Brombenzene.

Nitro compounds :—

Nitroethane.
Nitropropane.
Tetranitromethane.
Isobutyl nitrate.

Sulphur compound :—

Carbon bisulphide

Notes.

- (a) Gautier-Charpy, red-brown.
(b) Thiel-Krüss, wine-red; (xylenes not separated).
(c) Gautier-Charpy, Krüss-Thiel, red.
(d) Tetra-chlorethylene, C_2Cl_4 , is the only substance in the above list which is unsaturated in structure. Its easy formation during chlorination reactions indicates that its unsaturated character is more formal than real, in spite of its double bond.
(e) Ethylene bromide, amyl bromide, and isobutyl chloride required careful purification before giving violet solutions. The impure solvents, which gave red solutions, all decolorised permanganate.
(f) Gautier-Charpy, Krüss-Thiele, red.

B. Brown Solutions.

Iodides :—

Ethyl iodide.
Amyl iodide.
Cetyl iodide
Phenyl iodide
Potassium iodide } In water solutions.
Hydrogen iodide }
Oxygen compounds.

Alcohols :—

Methyl alcohol.
Ethyl alcohol.
n-Butyl alcohol.
Dimethylethyl carbinol.
Heptyl alcohol.

Ethers :—

Ethyl ether.
Dimethyl acetal.
Anisol.
Phenetol.

Ketones :—

Acetone.
Methylethyl ketone.
Diethyl ketone.
Acetaldoxime.
Acetophenone.

Acids and esters :—

Formic acid.
Acetic acid.
Lactic acid.
Caproic acid.
Ethyl acetate.
Amyl acetate.
Isobutyl isobutyrate.

Sulphur compounds :—

Amyl mercaptan.
Thiophene.
Nitrogen compounds.

Nitriles :—

Acetonitrile.
Propionitrile.
Capronitrile.
Benzonitrile.

Nitrilo-bases :—

Pyridine.
Quinoline.

From the results tabulated above, all of which have been verified personally, the relationship between colour and the constitution of the solvent stands out clearly; *saturated solvents give violet, solvents which have unsaturated character give brown solutions*. In the first, or violet class, we find hydrocarbons, their chlorides and bromides, and carbon bisulphide; and also, strange to say, the *nitro compounds*. All the other oxygen compounds, so far as investigated, give brown solutions. The brown solvents comprise the alcohols, ethers, ketones, acids, and esters; nitriles and nitrilo-bases; alkyl and other iodides; and bivalent sulphur compounds.

The iodine molecule, as found in iodine vapour, is violet; we have every reason for assuming that in its violet solutions iodine is in a state of normal physical distribution. On the other hand, certain of the brown solutions are known to contain periodides, usually of the form $(MX)_2I_2$; among these are potassium iodide, phenyl iodide, and the tertiary bases. Nitriles have long been known for their additive properties in general; and in the case of oxygen compounds, the recent startling results of Baeyer and Villiger (*Ber. d. Chem. Ges.*, 1901, xxxiv., 2679) have fully demonstrated the hitherto unsuspected additive powers of combined oxygen atoms. It seems quite justifiable to assume in all brown iodine solutions the existence of (probably unstable) addition products whose general composition is—

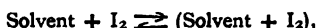


Such an explanation was indeed offered some years ago by Beckmann (*Zeit. Phys. Chem.*, 1889, v., 76), and considered and rejected by Krüss and Thiele. If it is assumed, as it was by Beckmann, that the whole of the iodine thus adds to the solvent, the effect upon the observed molecular weight would be a marked decrease (as a consideration of Raoult's formula shows), contrary to the measurements of Krüss and Thiele. But there is no need to make this assumption; a very small amount of alcohol suffices to change the colour of an iodine-chloroform solution, and 3 per cent of alcohol gives as dark a brown as can be obtained with pure alcohol.

Effect of Absolute Alcohol on Colour of Iodine in Chloroform.

Alcohol, per cent.	Colour.
3.5	Brown
0.4	Red
0.2	Mixed red and violet
0.1	Violet

The iodine in brown solutions is therefore probably in a condition of equilibrium between pure solution and the addition product—



very much like many double salts, or like the chlorine ions in green chromium chloride hexahydrate (Werner, *Ber. d. Chem. Ges.*, 1901, xxxiv., 1579).

The view here presented, that brown solutions contain some addition product, and violet solutions simple iodine molecules, is borne out by an important fact:—Brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently (Krüss and Thiele, *Comptes Rendus*, 1891, cxii., 72; Gautier and Charpy, *Comptes Rendus*, 1890, cxi., 645; Wiedemann, *Wied. Ann. Phys.*, cclxix., 580). As heat produces dissociation, and cold induces association, the facts are in excellent agreement with expectation.

The actual isolation of the addition products of iodine with oxygen compounds will probably be difficult, but an effort in this direction will be made as soon as possible. Schützenberger has described an addition product of bromine and ether, and iodine may behave similarly (*Comptes Rendus*, 1873, lxxv., 1511; *Lieb's Ann. Chem.*, 1873, clxvii., 86).

Two points remain for discussion. In the first place, the behaviour of the nitro compounds seems to put them apart from other oxygen compounds. The structure of the nitro group is still uncertain, but numerous reactions show that its oxygen atoms are quite active, and possess considerable additive power (Lachman, *Am. Chem. Journ.*, 1899, xxi., 443; *Journ. Am. Chem. Soc.*, 1901, xxiii., 897; Angeli, *Ber. d. Chem. Ges.*, 1896, xxix., 1884; Meisenheimer, *Lieb's Ann. Chem.*, 1902, cccxxiii., 205). Their indifference to iodine will be investigated more closely later on.

The second point is the behaviour of ethyl bromide towards iodine. In spite of numerous efforts, I have not been able to prepare this substance in a state sufficiently pure to obtain with it a violet iodine solution; in every case the solution is dark red. Ethyl bromide is made by two methods; the distillation of ethyl-sulphuric acid with potassium bromide also forms ether, which cannot be separated by the most careful fractioning; and the action of phosphorus bromide upon alcohol yields ethyl bromide contaminated with phosphorus, which resist hours of boiling with moist sodium amalgam. I am confident, however, that ethyl bromide will prove no exception to the above classification of iodine solvents, for similar difficulties were met, during this investigation, with amyl bromide and ethylene bromide. The first samples of these substances gave dark red iodine solutions, but after careful purification pure violet solutions were obtained.—*Journal of the American Chemical Society*, xxv., No. 1.

A GLASS-BLOWING "WRINKLE."

By F. S. LOCKE, M.A., M.D.

INSTEAD of using cork or rubber stoppers, or the cotton-wool plugs often improvised, for temporarily closing the ends of glass tubes requiring to be blown, I have for the last couple of years employed plugs formed as required of loose asbestos, which must be of the kind commercially known as "woolly." The proper amount for the particular case is rolled into a ball between the finger-tips and stuffed into the opening to be stopped with the aid of, e.g., a wooden match. The same asbestos can, of course, be used over and over again.

A much better seal is obtained—owing to the adhesive and cohesive quality of this material—than with cotton-wool, which it equals in ease of hasty application. Its unique advantage is the absence of all decomposition, blackening, charring, and consequent cracking, even when the glass is heated close to the plug.

I find that Threlfall ("Laboratory Methods," London, 1898, p. 27) recommends the employment of asbestos for annealing, but does not refer to the application of it here in question.

THE ELECTROLYTIC ESTIMATION OF SMALL QUANTITIES OF SILVER IN THE PRESENCE OF A LARGE AMOUNT OF LEAD.

By MM. ARTH and NICOLAS.

THE separation of lead and silver in nitric solution has been described already by several writers, notably by M. Luckow and by M. Riche. We know that lead is generally deposited in the oxidised form on the anode, and that the silver is obtained in the metallic state on the cathode.

We have taken up the examination of this question from a special point of view, which does not seem to have been studied yet, viz., the endeavour to determine the most favourable conditions for the easy estimation of small quantities of silver in the presence of large amounts of lead, and also to determine the limits to which the operation can be carried in a practical manner.

Lead is not deposited in the metallic form on the cathode in a solution containing sufficient free acid, and to be precipitated in the form of the binocide on the anode a large amount of free acid is necessary, and a fairly high electromotive force.

Silver, on the other hand, only requires moderately acid solutions and a relatively low electromotive force for its deposition. It has, however, the very inconvenient tendency of being deposited in the spongy form, which can only be avoided with certainty by not exceeding a certain voltage, as was shown by Kuster and Steinwehr for the separation of silver and copper, in which case 1.38 volts is the maximum to be used (*Zeit. für Electrochemie*, 1897-1898, p. 451). These two properties are fortunately concordant. It was obviously necessary to try and find if there was any definite electromotive force which would conveniently precipitate the silver contained in a solution of nitrate of lead, while leaving the latter metal intact.

After several attempts, we have decided definitely on a maximum tension of 1.1 volt. With 1.2 volt we can already detect the presence of a few grains of spongy metal on the edges of the cathode.

Further, the operation is only really practicable when we use a source of electricity giving 1.1 volt on an open circuit. Thus we may be certain of never surpassing the maximum indicated, even when the resistance of the bath becomes very great, and all checking of the current is useless; with a higher voltage it is almost impossible to obtain the desired result by introducing metallic resistances into the circuit, as is often done. Neither is it necessary to trouble about the quantity of the current, which is always very low.

No. of expt.	Silver in solution. Grm.	Lead in solution. Grms.	Ag : Pb.	HNO ₃ . C.c.	Alcohol. C.c.	Temperature.	E.M.F. Volts.	Total volume. C.c.	Time. Hours.	Silver found.	Differences.
1.	0.0108	2.5	1 : 231	2	6	60°	1.0	130	8	0.0108	0
2.	0.0054	2.5	1 : 462	2	6	60	1.0	130	6½	0.0056	+0.0002
3.	0.0054	5	1 : 924	2	6	60	1.1	250	6½	0.0054	0
4.	0.0054	10	1 : 1850	2	6	60	1.1	350	8	0.0052	-0.0002
5.	0.0054	20	1 : 3703	2	6	60	1.1	300	7	0.0054	0
6.	0.0054	40	1 : 7407	2	6	60	1.1	500	6½	0.0052	-0.0002
7.	0.0054	100	1 : 18,518	2	6	60	1.1	500	6½	0.0066	+0.0012
8.	0.0054	100	1 : 18,518	4	6	60	1.1	500	8½	0.0054	0
9.	0.0054	100	1 : 18,518	5	6	60	1.1	500	6½	0.0052	-0.0002

NOTE.—In Experiment No. 7 we found a little lead in the metal deposited on the cathode.

The volumes of the solutions to be electrolysed being generally very considerable, we use as the cathode the platinum gauze recommended by Winckler; for the anode we prefer either a thick platinum wire bent into a helix, or a small cylinder of sheet platinum pierced with several holes, having the same height as the cathode and a diameter of 15 m.m.

Our solutions were obtained by dissolving a definite weight of pure nitrate of lead in a known volume of distilled water, and then adding a titrated solution of nitrate of silver so as to introduce the desired quantity of the latter metal. We also added a few c.c. of pure concentrated nitric acid and 6 c.c. of alcohol at 95°. The whole was poured into a Bohemian glass vessel of suitable dimensions. Care must be taken not to add too little acid, otherwise a little lead might be deposited with the silver (see Experiment No. 7). A minimum quantity of acid of 1 per cent of the total volume appears to be a suitable amount.

At the ordinary temperature the deposit of silver is badly and incompletely effected; on the other hand, all goes easily and completely if we heat the liquor to 55–60°.

Under these conditions, the nitrate of lead remains almost inert; in certain cases only, when the solution is sufficiently concentrated, or the density of the current at the anode becomes relatively strong, we obtain a slight deposit of brown peroxide.

This circumstance is a very favourable one, as it enables us to operate in the presence of as great a weight of lead as we wish.

The duration of the operation is about seven hours; it is especially necessary to prolong the experiment sufficiently when extracting the silver from a considerable quantity of liquid. In such a case it is also indispensable to stir the solution frequently so as to bring all portions of it into contact with the electrodes.

In the accompanying table will be found a summary of a certain number of our experiments.

These results show that it is possible to extract small quantities of silver quantitatively, even from concentrated solutions of nitrate of lead, and, further, the process is sensitive, for it is evident that we could operate in the presence of still larger amounts of lead than those we have used; it would suffice to increase the quantity of free acid and the volume of the solution in a corresponding manner, or, if the amount of silver obtained in a preliminary experiment is too small to be weighed with sufficient accuracy, we could place the electrodes successively in several solutions of the same materials.

For the detection of silver in commercial lead (sheet lead), we proceed in the following manner:—The metal is first melted and run into sticks to get rid of the outer layer; we then dissolve 100 grms. in pure nitric acid diluted with water. The solution is evaporated to dryness on the water-bath to drive off the excess of nitric acid, and the salt is taken up with 500° c.c. of distilled water. After the addition of the nitric acid, and alcohol we electrolyse as above. The weight of silver found was 0.0042 grm., or one part in 23809.

This lead contained a small quantity of copper, but this

did not interfere at all, as copper is not deposited with such a low electromotive force. We have also made certain that bismuth is not deposited in the conditions under which we operated.

A second sample gave for 100 grms. of metal 0.0012 grm. and 0.0009 grm. of silver in two experiments, or practically one part in 100,000.

With a third sample of the commercial metal we found 0.0015 grm. of silver, or one part in 75,000.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 13.

VOLUMETRIC ESTIMATION OF THE LIME AND MAGNESIA SIMULTANEOUSLY PRESENT IN SOLUTIONS OF CHLORIDE OF SODIUM (BRINES FROM SALT-MARSHES).

By ALEX. D'ANSELME.

This method depends upon the use of NaOH mixed with CO₃Na₂ in titrated solution.

We have observed that the salts of magnesia in a saturated solution of common salt are completely precipitated by a solution of CO₃Na₂ mixed with a sufficient quantity of NaOH in the proportion of 4CO₃Na₂ to one of NaOH; this does not take place with CO₃Na₂ alone. This solution is titrated in the presence of tropeoline with molecular SO₄H₂; we then proceed as follows:—

1. The salts of lime and magnesia are estimated together.
2. The lime salt is estimated alone.
3. The amount of lime is deducted from the salts of lime and magnesia together, and the difference gives the amount of magnesia.

The volumetric data, given by operations 2 and 3, are transformed into grms. per litre corresponding to the salt of lime or magnesia, by multiplying the figures observed by 1.36 for sulphate of lime and by 0.95 for chloride of magnesia.

Method of Procedure.

1. *Simultaneous Titration of the Salts of Lime and Magnesia.*—Take 100 c.c. of the sample, and add 10 c.c. of the above solution; heat, filter, and titrate the filtrate, and the observed value deducted from the titration value of 10 c.c. of the solution added, will give by difference the value for the salts of lime and magnesia together.

Comparative Results obtained with a Raw Brine from a Salt-marsh.

	Degrees Baumé at 15°	..	24.7	
	Density at 15°	..	1.207	
NaCl	..	..	314.4	grms. per litre
SO ₄ Ca	volumetrically	..	2.720	" "
	gravimetrically	..	2.723	" "
MgCl ₂	volumetrically	..	0.750	" "
	gravimetrically	..	0.751	" "

2. *Titration of the Salt of Lime alone.*—Take 100 c.c. of the solution, and add 100 c.c. of 10 per cent chloride of ammonium, then 10 c.c. of the above mentioned titrated solution; this must not be heated for fear of completely decomposing the chloride of ammonium by means of the caustic soda. Filter, wash well, and titrate the filtrate; the difference between this value and that obtained with the lime and magnesia together will give the value of the magnesia.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

NOTE ON THE USE OF A NEW DENATURISING AGENT FOR COMMERCIAL ALCOHOLS.

By M. CARI-MANTRAND.

In the year 1895, I published in the *Moniteur Scientifique* a communication on the insufficiency of the present methods of denaturising commercial alcohols. In the course of this paper I showed that by special treatment it was possible to recover from alcohol denaturated by the official method,* at least 75 per cent of an alcohol suitable for purposes of consumption. The price of treatment, with the integral recovery of the denaturising substance, can be reduced to 12 francs per hectolitre.

In publishing this method I reserved to myself the right of communicating to the Consultative Committee of Arts and Manufactures a new denaturiser of more certain efficacy than the methylene or wood-spirit officially adopted. This substance, taken from among the series of methylic derivatives, offers the advantage of not being able to be separated by the fractional distillation of the ethylic alcohol, or by the method which I had used for the revivification of denaturated alcohol, a process also applicable to the elimination of all substances suitable for denaturising, such as heavy oils from coal-tar, pyrogenous oils, aromatic essences, &c.

Now, as the old method of denaturisation by methylene has been adhered to, in spite of its imperfections, I have abstained from mentioning my new denaturiser.

But as at the present time a commission has been appointed by the Minister of Finance to prepare a complete revision of the law on spirits and commercial alcohols, the moment appears to me to be opportune to state that in 1895 I recommended cyanide of methyl (acetoneitrile) boiling at 82°, density at 15°=0.819 as a good denaturising agent.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, December 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Com-

bustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford shows a deficit during the past month. The actual amount of rain measured during November was 1.47 inches; the average fall is 2.30 inches. Thus we have a deficit of 0.83 inch, which, if deducted from the previous excess of 12.57 inches, leaves a total excess for the year of 11.74 inches, or 50.7 per cent on the thirty-five years' average.

Our bacteriological examinations of 351 samples taken during last month have given the results recorded in the following table. Besides these samples we have examined 356 others from special wells, standpipes, &c., making a total of 707 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	845
New River, filtered (mean of 61 samples) ..	25
Thames, unfiltered (mean of 25 samples) ..	18,390
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 193 samples) ..	43
Ditto ditto highest	572
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	610
River Lea, from the East London Water Company's clear-water wells (mean of 23 samples)	28

Of the 277 daily samples taken from the filter wells of the Metropolitan Water Companies, eleven samples, or 4.0 per cent, were sterile. Thirty samples, or 10.8 per cent, contained more than 100 microbes, and of these, sixteen samples contained more than 150 microbes per c.c. The thirty excess samples contained an average of 168 microbes per c.c. In October fifty-one excess samples contained an average of 186 microbes per c.c. The above figures show that there has been a considerable improvement in the bacterial character of the impounded and filtered supply during the past month, although the condition of the crude water taken from the Rivers Lea and Thames was worse than during October.

The soluble organic matter in the supply derived both from the Lea and Thames has been steadily diminishing during the course of the month. The brown colour also has become less.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

The Central.—Under this title there has just been published the first number of a new monthly magazine, edited on behalf of the Committee of the City and Guilds of London Central Technical College Old Students' Association, by Dr. E. F. Armstrong and M. Solomon. The two principal aims of the editors are, firstly, to produce a magazine which will be of interest to the Central Students, past, present, and future, and, secondly, to produce a magazine worthy of the college, and which shall serve as a permanent record of the valuable work it is doing. We congratulate the editors on the excellent literary character of the first number of their new venture. It is well printed on good paper, and has an excellent portrait of Prof. W. C. Unwin as frontispiece. The only fault we have to find is with the abominable wire-binding. Such a form of binding should never be used for any book which is intended to be read; it makes the holding of the volume troublesome and tiring, and many people will not look at a magazine or book fastened up in this style.

* Circular of June 25, 1873, No. 61; formula for denaturisation:—
Alcohol at 90° 100 litres
Methylene 15 "
Heavy benzine (boiling-point 150–200°) .. 0.5 "
Malachite green 2 grms.

ACTION OF METALLIC MAGNESIUM UPON
AQUEOUS SOLUTIONS.*

By LOUIS KAHLENBERG.

It has long been known that metallic magnesium acts extremely slowly upon distilled water, and that it practically does not act at all upon solutions of the caustic alkalis. In 1899, Tommasi (*Bull. Soc. Chim.*, 1899, [3], xxi., 885—887) made qualitative investigations of the action of magnesium on aqueous solutions of the following salts:—KCl, NH_4Cl , CaCl_2 , MgCl_2 , NaCl, LiCl, BaCl_2 , SrCl_2 , CuCl_2 , CdCl_2 , PbCl_2 , HgCl_2 , FeCl_3 , CrCl_3 , PtCl_4 , AuCl_3 , CuSO_4 , ZnSO_4 , FeSO_4 , MnSO_4 . He found that from solutions of sodium, potassium, and lithium chloride, magnesium liberates hydrogen more rapidly than from pure water, magnesium hydroxide being formed. Solutions of the chlorides of barium, strontium, and calcium were acted upon but feebly by magnesium, but ammonium chloride solution was attacked at a lively rate. From solutions of the salts of the heavy metals mentioned above, hydrogen was liberated by magnesium, the chloride or sulphate of that metal being formed, and a basic salt or hydroxide of the heavy metal, or the latter in the metallic state, precipitated. No theoretical explanations were attempted. In the same year, G. Lemoine (*Comptes Rendus*, 1899, xxix., 291) called particular attention to the action of magnesium upon aqueous solutions of magnesium salts. He used solutions of the nitrate, chloride, sulphate, and acetate of magnesium, but worked especially with the last three salts. From aqueous solutions of these salts, magnesium liberates hydrogen rapidly and continuously. Using magnesium in form of powder, he found that about 0.4, the calculated amount of hydrogen, was liberated from a magnesium chloride solution when the powder was present in excess, the action being finally checked by the accumulation of the precipitate formed; but up to the maximum, the quantity of hydrogen disengaged was nearly proportional to the amount of magnesium added. After magnesium had acted upon the solutions of the chloride and acetate, these were found to contain but a relatively slight excess of the base. The analytical data show that the precipitates formed were very basic chloride and acetate of magnesium respectively. In the case of the magnesium sulphate the solution was much weaker after the magnesium had acted upon it, a very considerable portion of the salt having been thrown down in combination with the magnesium hydroxide in form of a basic sulphate of magnesium. Lemoine's explanation of the action of magnesium on solutions of magnesium salts is that in these solutions the salts are slightly decomposed into magnesium hydroxide and free acid. This acid acts on the metal, forming hydrogen and a basic salt which breaks up into the normal salt and hydroxide of magnesium; the latter finally drops out of solution and the reaction begins anew. In advancing this explanation it would certainly seem that Lemoine did not give due weight to the fact that the reaction of the solutions of the magnesium salts towards indicators is perfectly neutral at the outset, and that soon after introducing the magnesium it becomes alkaline and remains so, while the liberation of hydrogen continues unabated. There are thus no facts upon which to base the assumption that the salts he used are even slightly decomposed by water into free acid and magnesium hydroxide.

H. Mouraour (*Comptes Rendus*, 1900, cx., 140) again directed attention to the fact that magnesium liberates hydrogen readily, not only from solutions of its own salts, but from solutions of other salts as well. He found solutions of the carbonate, chloride, oxalate, and sulphide of ammonium strongly acted upon; but no action was observed in the case of a solution of ammonium fluoride.

Sodium carbonate, acetate, and tetraborate solutions were strongly acted upon, as were also solutions of ordinary and chrome alum. On the other hand, the action was feeble on solutions of sodium phosphate, nitrite, thiosulphate, potassium ferrocyanide, and the chlorides of barium, calcium, and potassium. The work was entirely qualitative in character. Mouraour states that while Lemoine's explanation of the action may hold good in the case of solutions of chloride of magnesium, for instance, for the most of the salts last mentioned it is inadequate. In the case of the ammonium salts, Mouraour ascribes the action to the fact that solutions of these salts dissolve magnesium hydroxide. But he states that in the case of the salts of lead, copper, mercury, and cobalt, from which magnesium precipitates the heavy metals and simultaneously liberates hydrogen, we have a secondary action of the magnesium on the water of the solution. He deems it very difficult to explain the phenomena in the cases last mentioned, stating that it is not probable that salts of these heavy metals favour the solubility of magnesia. Mouraour was apparently not aware of the work of Tommasi. As a matter of fact, magnesium hydroxide is not formed at all when solutions of the heavy metals named are acted upon by magnesium; the salt of the latter metal forms and remains dissolved, the basic salt or hydroxide of the heavy metal being precipitated. In fact, the cases which Mouraour finds difficult to explain are really most readily explained, for the salts of the heavy metals are indeed slightly decomposed by water, a small quantity of free acid being liberated, as the acid reaction of such solutions clearly shows. This acid acts on the magnesium, evolving hydrogen and forming the corresponding magnesium salt, a basic salt or hydroxide of the heavy metal resulting simultaneously.

In presenting to my students the various ideas that have from time to time been entertained by scientific men regarding the nature of solutions, I have always laid considerable stress upon the view that the process of solution depends upon a mutual interaction of solvent and solute and that solutions are chemical combinations[†] of solvent and solute according to variable proportions. Although this view has of recent years been relegated to the background by many, it certainly has a formidable array of facts to support it; and such facts have really been accumulating more and more, though the investigations yielding them have been guided to a considerable extent by the analogy between gases and solutions. If when a substance is dissolved in water chemical combination between that substance and water takes place, the liberation of hydrogen from the solution ought to result with a different degree of readiness than from pure water. With this as the guiding idea, Mr. O. W. Brown and Dr. H. V. Black at my suggestion made some preliminary experiments in this laboratory last summer, comparing the rate with which hydrogen is evolved from various aqueous solutions by the action of magnesium upon them. In the course of these experiments (among which many of the observations of the above named French investigators were confirmed, though at the time their researches had not been looked up) it was found that hydrogen was liberated with different rapidity in the case of each solution tested, and that this rate was different from that observed when pure water was used. To my regret Messrs. Brown and Black were unable to continue these investigations, much as they were inclined to do so. It seemed to me well worth while to follow out somewhat further the work thus begun and the results obtained in investigating the subject will now be presented.

The metallic magnesium used was of Schuchardt's manufacture. It was carefully tested, and was found to be free from carbon, and from alkali and alkaline earth metals. 0.8593 grm. of the metal yielded 0.0036 grm. of the mixed

* Read at the Washington Meeting of the American Chemical Society, and at the meeting of the Wisconsin Academy of Sciences, Arts, and Letters at Madison, December 26, 1903. From the *Journal of the American Chemical Society*, xxv., No. 4.

† Compare Mendeleeff, "Principles of Chemistry," vol. i.; Pickering on Solutions; Watts' "Chemical Dictionary"; Horstmann, Graham-Otto, "Lehrbuch der Physikalischen und Theoretischen Chemie," vol. II.

TABLE I.

(Solutions contain 2 grm.-mols. per litre, except the mannite and sodium sulphate solutions, which contain 1 grm.-mol. per litre).

Solute.	2½ hours.	23½ hours.	47½ hours.	53 hours.
Distilled water (alone)	0'02	0'10	1'5	1'8
Alcohol	0'10	0'40	7'6	7'8
Glycerin	0'01	0'05	0'5	0'55
Cane-sugar	0'10	0'65	1'0	1'2
Mannite	0'08	0'20	0'4	0'55
Urea	1'2	10'6	29'0	31'0
Sodium chloride	7'4	49'8	Discontinued (a)	
Sodium sulphate	2'4	9'9	18'0	18'8

TABLE II.

(Solutions contain 1 grm.-molecule per litre).

Solute.	25 mins.	40 mins.	50 mins.	1 hour.	1 hr. 20 min.	1 hr. 35 mins.	2 hrs. 56 mins.	4 hrs. 23 mins.
MgCl ₂	13'0	18'5	22'0	24'8	30'5	33'8	Discontinued.	
MgBr ₂	4'8	7'0	8'5	9'9	13'0	14'8	24'5	33'4
MgSO ₄	5'9	9'4	11'6	13'75	18'5	21'5	36'4	50'5
Mg(NO ₃) ₂	0'2	0'35	0'4	0'45	0'6	0'65	1'2	1'6

TABLE III.

(Solutions contain 1/10 grm.-mol. per litre).

Solute.	25 mins.	35 mins.	3 hours 31 mins.	4 hours 5 mins.	5 hours 32 mins.	22 hours 34 mins.
MgCl ₂	10'8	14'0	43'1	47'6	Discontinued.	
MgBr ₂	1'8	2'4	7'9	8'6	10'3	25'0
MgSO ₄	1'8	2'4	7'9	8'6	10'3	27'0
Mg(NO ₃) ₂	0'2	0'3	1'7	1'8	2'2	3'6

TABLE IV.

(Solutions contain 1/100 grm.-mol. per litre).

Solute.	17 mins.	31 mins.	45 mins.	49 mins.	2 hrs. 25 mins.	3 hrs. 37 mins.	5 hrs. 25 mins.	22 hrs. 49 mins.
MgCl ₂	1'8	3'2	4'7	5'2	12'2	15'6	20'0	43'0
MgBr ₂	1'4	2'0	2'6	2'8	5'8	7'1	9'6	20'9
MgSO ₄	1'5	2'4	3'0	3'2	6'8	8'8	11'6	29'6

TABLE V.

(Solutions contain 1 grm.-mol. per litre).

Solute.	17 mins.	31 mins.	45 mins.	49 mins.
KCl	11'5	17'5	22'5	24'0
KCl+MgCl ₂	15'0	23'0	29'4	31'4

TABLE VI.

(Solutions contain 1/10 grm.-equivalent per litre).

Solute.	2 mins.	4 mins.	6 mins.	11 mins.	16 mins.	28 mins.	33 mins.	36 mins.	46 mins.
H ₂ SO ₄	3'2	8'0	12'0	21'0	28'0	37'6	40'4	41'8	45'6
Solute.	1 min.	3 mins.	5 mins.	7 mins.	11 mins.	14 mins.	24 mins.	29 mins.	49 mins.
HCl	3'0	8'5	14'0	19'0	27'5	31'4	39'4	43'5	48'8

(Solutions contain 1/100 grm.-equivalent per litre).

Solute.	5 mins.	10 mins.	17 mins.	20 mins.	30 mins.	40 mins.	1 hour 5 mins.	1 hr. 20 mins.	3 hrs. 37 mins.
H ₂ SO ₄	0'4	1'2	2'0	2'5	3'6	4'6	7'0	8'4	14'3
HCl	0'4	1'2	2'0	2'5	3'6	4'7	7'0	8'0	11'8

(a) The word "discontinued," when used in the tables, means that the experiment was discontinued, not that the hydrogen ceased to be evolved. The experiments in these cases had to be stopped because more gas could not be held in the tube used.

sesquioxides of iron and aluminium. Other metals were not present in the magnesium. The latter was cut into bars of square cross-section measuring 5 m.m. on an edge, and having a length of 57·5 m.m., thus presenting a surface of 1200 sq. m.m. A large number of such bars were prepared. In each liquid to be tested, such a bar was immersed, its surface being first carefully cleaned with fine emery cloth. The action of the metal upon the liquid was

noted and the volume of hydrogen evolved at different times was observed. The experiments were conducted at room temperature which was nearly 20°. The ordinary distilled water of the laboratory was used. The chemicals were either of Kahlbaum's or Schuchardt's manufacture; they were tested as to their purity, special care being taken to see that they were free from traces of heavy metals, and in the case of the salts employed, that they were perfectly

neutral. Although only one series of results will be given in each case, each series was checked by at least one additional independent series. In the accompanying tables, the first column indicates the solute employed; the heading of each succeeding column indicates the time that a bar of magnesium acted upon the solution in order to liberate the volume of hydrogen given in that column (cubic centimetres).

In the case of the urea solution, ammonia as well as hydrogen was liberated. When sodium nitrate solution is treated with magnesium, only a slight amount of hydrogen is actually evolved; this is due to the fact that the salt is reduced to nitrite. From a solution of ammonium chloride containing 2 grm.-mols. per litre, over 50 c.c. of gas, consisting of hydrogen and ammonia, were liberated by one of the bars of magnesium in five minutes.

It was found that in normal potassium or sodium hydroxide solutions no measurable amount of hydrogen was evolved in twenty-four hours, the magnesium remaining perfectly bright. Solutions of magnesium nitrate when treated with magnesium yield nitrite, and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From solutions of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate solution was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. From a solution of crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in glycerin of 1.27 sp. gr., magnesium evolves hydrogen; the action is much increased upon heating. Anhydrous magnesium chloride (prepared from the double magnesium ammonium chloride) dissolved in glycerin of 1.27 sp. gr. acts slowly on magnesium; this action is greatly increased upon raising the temperature. The glycerin itself acts only very slightly on magnesium even on heating. From $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ melted in its crystal water, magnesium evolves hydrogen readily. A saturated solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in ether does not attack magnesium. From a solution of 1 grm.-mol. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 99.5 per cent alcohol a bar of magnesium, of the size above described, evolved 2.5 c.c. hydrogen in twenty-three hours and forty-seven minutes, while from 99.5 per cent alcohol alone a like bar of magnesium liberated 0.9 c.c. gas in twenty hours and forty-four minutes. Table I. shows that from distilled water there was evolved under like conditions only 0.1 c.c. in twenty-three and a-half hours.

The results in Table I. show that during the first twenty-three and a-half hours all the solutions except that of glycerin act more vigorously on magnesium than on water alone. Throughout the experiment the glycerin solution lags behind water. After forty-seven and a-half hours, more gas has been evolved from the water than from the solutions of glycerin, sugar, and mannite, and the same holds true after fifty-three hours. It is especially interesting to note that the alcohol solution is much more vigorous in its action on magnesium than is pure water. The urea solution is relatively vigorously attacked, though, as has been stated, ammonia is also formed in this case. Again, sodium chloride solution is much more vigorous in its action than sodium sulphate solution of equivalent strength.

Tables II., III., and IV. show that magnesium evolves hydrogen from solutions of magnesium salts at a fairly rapid rate. The solutions of the magnesium chloride are the most vigorously attacked in all cases. In the solutions containing 1 grm.-mol. per litre (Table II.) the sulphate solution is acted upon more vigorously than that of the bromide; in the solutions containing 0.1 grm.-mol. per litre (Table III.) hydrogen is evolved from the bromide and sulphate solutions at an equal rate for about five hours, within the limits of experimental error, while in the solutions containing 0.01 grm.-mol. per litre (Table IV.) hydrogen is again evolved more rapidly from the sulphate solution than from that of the bromide. In the solution of nitrate of magnesium, nitrite is formed, as mentioned above, which

accounts for the fact that but little gas appears in the case of this salt. Table V. shows that the potassium chloride solution containing 1 grm.-mol. per litre acts fully as vigorously as a magnesium chloride solution of 1 grm.-mol. per litre. The double potassium-magnesium chloride acts still more strongly, as the table indicates. The observation that potassium chloride solutions act readily on magnesium agrees with that of Tommasi; Mouraour called the action feeble.

At my request, Mr. W. R. Mott measured the so-called single differences of potential between magnesium and some of the salt solutions in question. The measurements were made against the normal calomel electrode, the potential of which was taken to be -0.56 volt. He found that at 20° C. the single potential between magnesium and sodium chloride solution (2 grm.-mols. per litre) is +1.163 volts; between magnesium and sodium hydroxide (1 grm.-mol. per litre) +1.111 volts; between magnesium and potassium hydroxide (1 grm.-mol. per litre) +1.140 volts; between magnesium and potassium hydroxide (0.1 grm.-mol. per litre) 1.105 volts; and between magnesium and magnesium sulphate (1 grm.-mol. per litre) +1.366 volts. Each result represents the average of four determinations, in which different bars of magnesium were used. In the sodium chloride solution, the electromotive force changes but slightly with the time; in the caustic alkali solutions, the electromotive force tends to fall with lapse of time; while in the magnesium sulphate solution, the electromotive force increases on standing.

The explanation of the above-described phenomena of the action of metallic magnesium upon aqueous solutions will now be considered. In the case of the saline solutions, one might feel inclined to assume that the salt acts upon the water, liberating a certain amount of free acid which attacks the magnesium, resulting in the liberation of hydrogen and the formation of a normal or basic salt or hydroxide of magnesium, according to the nature of the solution under treatment.* This would be an attempt to extend Lemoine's interpretation of the action of magnesium upon aqueous solutions of its salts to all aqueous saline solutions. As stated above, there is ground for this explanation in the case of salts of the heavy metals, whose aqueous solutions, as is well known, have acid reactions, indicating that they are indeed slightly decomposed by water, yielding free acid. But in the case of salts of Mg, Ca, Ba, Sr, K, Na, Li, there is no experimental evidence upon which to base the assumption that in their aqueous solutions there is any free acid present. Moreover, an alkaline reaction is imparted to the solutions of these salts by the magnesium soon after it has been immersed in them, and yet this alkalinity does not interfere with the evolution of hydrogen.†

There are no facts upon which to base the assumption that magnesium chloride in aqueous solution suffers greater hydrolytic decomposition (of which free hydrochloric acid is one of the products) than do the chlorides of calcium, barium and strontium for instance; and yet solutions of the last three salts are acted upon but feebly by magnesium, while from the magnesium chloride solution hydrogen is rapidly evolved. This point is illustrated still more strikingly by the fact that solutions of sodium and potassium chlorides are relatively strongly attacked by magnesium; what reasons are there to assume that these salts are decomposed more by water than those of the alkaline earth metals? And again, would it be rational to suppose that because potassium chloride solutions attack magne-

* In the language of the dissociation theory, preferred by some, it would mean that in saline aqueous solutions, from which magnesium liberates hydrogen more readily than from pure water, the salt reacts upon the water slightly, liberating some free acid, which in turn is electrolytically dissociated, yielding free hydrogen ions. The concentration of hydrogen ions in such solutions would then be greater than in pure water (which is supposed to be only slightly electrolytically dissociated), and this would account for the more vigorous action of magnesium upon saline solutions.

† According to the dissociation theory, such an alkaline solution would contain fewer hydrogen ions than pure water, and yet hydrogen is evolved faster from them than from water.

sium more readily than sodium chloride solutions, the former salt is decomposed more by water than the latter? But the difficulty of this mode of explanation becomes even greater in the case of the non-saline solutions. So, for instance, the alcoholic solution is acted upon more vigorously than pure water; clearly there is no chance for assuming free acid to be the active agent in the case of this solution.*

The idea that Mouraour advances in the case of solutions of ammonium salts, namely, that the solubility of magnesium hydroxide in them determines the liberation of hydrogen from them by action of magnesium, might possibly be applied to other solutions and so the attempt be made to generalise this explanation. In addition to the ammonium salts, there are several cases that might be considered to favour this view. So magnesium hydroxide is less soluble in solutions of sodium and potassium hydroxide than in pure water, and the fact that these solutions do not attack the metal as much as does water might be regarded as a support for the view advanced. Again, since ammonium fluoride solution is not acted upon by magnesium, and since the hydroxide and the fluoride of magnesium are insoluble in a solution of ammonium fluoride, this might be urged as another striking instance of the same kind. It would, however, be a delusion to think that the insolubility of magnesium hydroxide in these solutions is what prevents the magnesium from acting upon them. This becomes evident from the following experiment. On making magnesium amalgam (by heating magnesium and mercury together) and treating normal solutions of potassium and sodium hydroxide with the same, I found that hydrogen is very rapidly evolved, magnesium hydroxide formed, and mercury set free from the amalgam. Solution of ammonium fluoride is also violently attacked by magnesium amalgam with the concomitant liberation of hydrogen. Mere contact of magnesium and mercury in these solutions will not bring about this action; the amalgam must be used.

At a given temperature and pressure the course that a chemical reaction will take is determined (1) by the chemical affinity between the reacting substances, and (2) by the relative masses of these substances. If the system consists of a solid immersed in a liquid, the rate of action depends on the amount of surface of the solid exposed to the liquid. If the product is an insoluble one and closely envelops the surface of the solid that is being acted upon, the rate of the action will be diminished because of diminution of the surface exposed. This effect of the accumulation of the insoluble product of the reaction increases, the longer the reaction goes on, and may finally practically check the process, which is clearly shown by the results of Lemoine cited above. While there can be no doubt of this effect, nevertheless the differences in the rates of evolution of hydrogen during the times recorded above are in general too great to be accounted for solely on the basis of accumulation of the precipitate. Of this I became especially convinced by treating aqueous solutions with sodium amalgam; in these cases, where no precipitate forms, similar large differences in the rate of evolution of hydrogen occur.† Again it is well to bear in mind in this connection, that during the time of duration of the above experiments but small quantities of magnesium hydroxide or basic magnesium salts were formed; in fact, in many cases a pre-

cipitate was not at all discernible. I assured myself that from a bar of magnesium that had remained in a normal solution of sodium chloride long enough to be visibly covered with a white coating, hydrogen was nevertheless much more rapidly evolved than from a fresh bar of magnesium just placed in water.

One might further be inclined to ascribe the action of magnesium on these aqueous solutions to mere contact action, *i.e.*, to so-called catalytic action of the solute or some of its ingredients, Tommasi (*loc. cit.*) states that in the case of the potassium chloride solution we apparently have the best instance of such contact action, for here the potassium chloride remains unchanged and the magnesium hydroxide only is formed. Nevertheless even here it is not an easy matter to free the latter from "adhering chlorides" by washing. It would scarcely be helpful to dismiss the matter by saying that in these diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when the hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water.

All the facts above presented are very readily explained on the basis of the view of solutions which suggested this research; namely, that solutions are chemical combinations of solvent and solute according to variable proportions.* It is clear that if water is chemically bound to the substance dissolved in it, the readiness with which metallic magnesium or sodium amalgam will liberate hydrogen from different solutions will in general be different. Again, the difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigorously attacked than in solutions in which the action is slight. The experimental data are in accord with this. If the chemical affinity existing between magnesium and the solution (regarded as a chemical combination of solvent with solute) is sufficient to overcome the cohesion of the magnesium, the latter is attacked; from the resulting compound hydrogen splits off, and the rest may all remain as a homogeneous liquid (*i.e.*, all may remain dissolved) or further decomposition into a precipitate, the hydroxide or basic salt, and a solution may occur, and usually does occur, after the action has progressed for a sufficient time. If no precipitate forms, the rate of change is not diminished by a decrease of the surface of metal exposed, and so the reaction is apparently aided. The more readily the dissolved products are removed from proximity of the surface of the metal by diffusion aided by mechanical stirring of some kind, the more rapidly the change progresses. Usually, as the gas is rapidly evolved, the liquid receives considerable stirring from this source. If the specific attraction called chemical affinity existing between magnesium and the solution is not sufficient at the temperature of experiment, to overcome the cohesion of the magnesium, no action will take place, as in normal potassium hydroxide solution for instance; if the affinity is barely able to overcome the cohesion, the action will go on very slowly, as in the case of water. As stated above, magnesium amalgam does act on normal potassium hydroxide solution with vigour, liberating hydrogen, forming magnesium hydroxide, and setting mercury free. The explanation of the action is similar to the one just given. Here the affinity between the solution and the amalgam is sufficient to disintegrate the latter, and magnesium hydroxide forms in spite of the fact that it is difficultly soluble. Under the conditions of the experiment, it is evidently easier to abstract magnesium from magnesium amalgam than to overcome the cohesion of pure magnesium. This is in harmony with the fact that magnesium amalgam does not form when magnesium and mercury are

* Indeed from the standpoint of the dissociation theory one would have to hold that the alcohol solution contains fewer hydrogen ions than are present in pure water, and hence action ought to be less than in the latter. Moreover from the point of view of this theory, magnesium ought to act rather less on solutions of magnesium salts, for the presence of magnesium ions would militate against the formation of more of them. And again, the difference of potential between magnesium and a magnesium sulphate solution ought to be less than between magnesium and a sodium chloride solution; the facts show that just the opposite is true.

† This most interesting problem of the action of alkali metals and their amalgams upon aqueous solutions is being studied in this laboratory by Mr. Gustav Fernekes at present. His work is already well advanced.

* The view that solutions are chemical combinations according to variable proportions, does not detract one particle from the law of definite proportions which is well established in the case of so very many compounds. Horstmann (*loc. cit.*) presents the whole matter so well that it is unnecessary to dwell further upon it here.

brought together at ordinary temperatures,* it requires a higher temperature in order that the union of the metals will take place.

The view that solutions are chemical combinations of solvent and solute may seem somewhat antiquated at the present time when purely physical conceptions of solutions are in predominance. But this older view is still held by eminent chemists and physicists, for it gives an adequate cause for the process of solution, for the thermal changes accompanying the latter, and for the fact that (exclusive of the mass) the properties of a solution are never found to be quite equal to the sum of the properties of solvent and solute. Moreover, facts known at present concerning both dilute and concentrated solutions are entirely compatible with it, and it will no doubt prove a most valuable aid in further research.

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

Ordinary Meeting, December 8, 1903.

Prof. A. K. HUNTINGTON in the Chair.

DR. LEHFELDT gave a short résumé of his paper on "The Total and Free Energy of the Lead Accumulator."

The most convenient form in which to express the concentration of acid in the accumulator, for the present purpose, is by the molecular function (Z) of H_2SO_4 . The heat of the reaction (in equivalents),—



may then be put in the form—

$$x - \frac{dQ}{dZ};$$

where x is the heat of reaction between the pure materials (in absence of water) and Q is the heat of formation of the mixture $Z.H_2SO_4 \cdot (1-Z)H_2O$. Numerical values of this are calculated from the experimental data already in existence for the range $Z=0$ to $Z=0.25$, and the results shown by a curve. The free energy can be put in a similar form. A curve is drawn for it, based on E.M.F. measurements, and the latter are compared with the vapour pressures (p) of dilute H_2SO_4 by the thermodynamic relation that takes the form—

$$\log p = \frac{F}{RT} \{fE \cdot dx - Ex\}$$

(F = Faraday, R = gas-constant, E = E.M.F., T = absolute temperature).

Dr. OGG sent in a short note in which he tested the numbers derived from Thomsen's formula, and compared them with those derived from Pickering's experiments. The former all lie below the latter, probably because the Thomsen formula does not absolutely represent the heat of mixture of H_2SO_4 and H_2O .

Dr. LOWRY made some remarks on the basis of the sulphate theory, observing that sulphating is usually looked upon as a "disease."

Dr. LEHFELDT, in his reply, said that the adoption of the sulphate theory was justified by the fact that measurements of the changes of weight in the Pb , PbO_2 , $PbSO_4$, and H_2SO_4 agreed tolerably closely with those deduced from the equation given in the paper. Sulphating, however, was not the same as the formation of sulphate during discharge, where only a film is allowed to form, and is immediately broken down by the current.

* At ordinary temperatures the affinity between these metals is not able to overcome their cohesions. Compare the work of Wanklyn and Chapman on magnesium amalgam in the *Journ. Chem. Soc.* [2], iv, 141.

Mr. J. A. SUTHERLAND, F.I.C., F.C.S., read a paper entitled "Bitumen in Insulating Compositions" (Part I.).

The author points out that little or no reliable data have been published as to the use of bitumen for electrical purposes. The chief source of bitumen is Trinidad Lake, where there is estimated to be a quantity of nine million tons, which appears to be renewed to the extent of 20,000 tons annually. Upwards of 150,000 tons are exported yearly. Bitumen is also found in Venezuela, California, and on the shores of the Dead Sea; it occurs in some limestone (asphalt) as an impregnation, about 10 to 15 per cent being present, but it does not pay to extract it from this source. Its physical and chemical properties and constitution, which are fully dealt with in the paper, prove it to be infinitely superior to gas or coal tar for insulation and durability. Care should be exercised in refining; the temperature should be regulated, or the results will be injurious both for paving and electrical purposes. It is used in cable insulation, and very extensively for joint boxes and troughs for "solid laid" cables. No specification is, however, in use, and the object of this paper is to invite discussion and the views of electrical engineers to assist the author in the completion of his experiments, and to enable him to draw up a satisfactory definition of bitumen, so that users may secure the best results from its valuable non-hygroscopic and insulating qualities.

Mr. GASTER referred to Roumanian sources of asphalt. He had succeeded in freeing pitch from its carbon, which could then be used for arc carbons and electrodes, but the pitch still retained too much oxygen to be a satisfactory substitute for bitumen.

Dr. STEINHART strongly supported the author in his remarks regarding the desirability of arriving at some standard tests for bitumen. Physical, as well as chemical and electrical tests were required.

Mr. E. KILBURN SCOTT said that some firms declare that refined pitch is as satisfactory as bitumen. Leakage troubles, especially where cables are laid in round curves, are often caused by the creeping of the cable—which can be prevented by the use of wooden bridges—and is not at all the fault of the filling-in material.

Papers by Mr. COWPER-COLES and Dr. PERKIN were held over, on account of the lateness of the hour, until the next meeting.

NOTICES OF BOOKS.

Knowledge Diary and Scientific Handbook for 1904. London: Knowledge Office. 1903. Pp. 108.

THE fourth volume of the "Knowledge Diary" has been compiled with the same care as the preceding ones. The articles contributed to the volume are of an eminently practical nature, and will be of value for purposes of reference. They deal with "The Camera Applied to Science," "Practical Meteorology," and various astronomical subjects. The diary portion of the volume is as usual arranged for one day on each page, with a few extra sheets at the end of each month for monthly notes.

Subject List of Works on Mineral Industries and Allied Sciences in the Library of the Patent Office. London: Darling and Son, Ltd. 1903. Pp. 302.

THIS subject list is No. 13 of the Patent Office Library series, and is arranged according to the same manner and system as the preceding subject lists that have been already noticed in this column.

The present volume comprises 2559 works (243 serials, 2316 text-books, &c.), representing some 5662 volumes. The catalogue entries relating to these works number 3257, and are distributed under 418 headings and sub-headings.

CORRESPONDENCE.

COCOANUT OIL IN MARGARINE.

To the Editor of the Chemical News.

SIR,—It may interest some of your readers, especially those who are Public Analysts, to know that there are margarines now on the market evidently containing cocnanut oil, the fat of which has a high specific gravity, a low Valenta degree, and a refraction with the butyro-refractometer corresponding with that of genuine butter fat; hence this instrument is rendered quite useless for their detection. The following are two samples that have just come under my notice :—

Specific gravity at 100°/100° F..	911·3	909·7
Reichert (5 grms.)	4·3	4·5
Valenta turbidity test	74° C.	79° C.
Butyro-refractometer at 30° C...	50°	47·5°

—I am, &c.,

E. W. T. JONES.

Wolverhampton.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 21, November 23, 1903.

Colour of Aqueous Solutions of Methyl-orange, and the Changes which occur during the Estimation of Acids.—P. Vaillant.—It is known that aqueous solutions of methyl-orange, which normally are yellow, change rapidly to red when in contact with acids. The author finds that the molecular absorption of aqueous solutions of methyl-orange is independent of the concentration. A series of coefficients of absorption are given for different degrees of concentration obtained by Gouy's spectrophotometer. The numbers given show that the molecular conductivity of the solutions are relatively considerable—being more than half that of HCl, and four times that of C₂H₄O₂. It must be admitted that aqueous solutions of methyl-orange only contain the two ordinary elements of electrolytic solution, a complete and a dissociated molecule, and that these two elements have the same yellow colour. The change of colour under the action of acids is progressive, and tends—as the quantity of acid increases—towards a limit which is independent of the nature of the acid, but is attained more rapidly with a stronger one.

Methods of Deformation and Rupture of Irons and Soft Steels.—F. Osmond, Ch. Frémont, and G. Cartaud.—The authors determine and classify the methods of deformation of the iron in various irons and soft steels.

Influence of Gases on the Separation of Metals by Electrolysis. Separation of Nickel and Zinc.—MM. Hollard and Bertiaux.—Metals whose polarisation tensions are higher than those of hydrogen (Zn, Cd, Fe, Co, Ni, Sn, and Sb) cannot practically be separated successively by a gradual increase of the electric tension of the electrodes, even though theory indicates that each metal ought to be deposited at one particular tension, called its polarisation tension. This non-agreement between theory and practice is, however, only apparent. It is true only when the solution offers great resistance and the current is feeble for the electric tension used. This current, which precipitates one of the metals at the cathode, precipitates also the hydrogen from the solution, so that a fraction only of the current is used for the deposition of the metal—a fraction much too feeble to determine complete separation.

The bath owes its great resistance chiefly to the evolution of hydrogen at the cathode and of oxygen at the anode. By suppressing one or other of these gases the author obtains a current strong enough to cause the separation of metals. The suppression of oxygen at the anode by the use of a soluble anode allows of the separation of nickel and zinc, whilst the suppression of the hydrogen at the cathode by the use of a tin or cadmium cathode allows of the separation of nickel and zinc.

Oxalacetic Acid.—L. J. Simon.—Oxalacetic acid, CO₂H—CH₂—CO—CO₂H, can be obtained by saponification of its ether by means of concentrated hydrochloric acid. It does not differ in its essential properties from that which Fenton, on the one hand, and Wohl, on the other, obtained by different methods.

Union of Dinaphthopyryl Salts with Phenols.—R. Fosse.—The dinaphthopyryl radicle, $\text{CM} < \text{C}_{10}\text{H}_6 > \text{O}$, can substitute its atom of hydrogen for a phenol radical, giving a body of formula $\text{O} < \text{C}_{10}\text{H}_6 > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{zOH}$. These derivatives of pyrene with phenol function can be obtained by the action of the chloride, bromide, or sulphate of dinaphthopyryl on the sodium phenols. The author investigates the reactions and properties of the series of derivatives formed.

Synthesis of Nicotine.—Amé Pictet.—The author discovers a synthesis of nicotine, starting from nicotinic acid and performing the following reactions :—Nicotinic acid is etherified, then transformed by means of ammonia into an amide, then treated with sodium hypobromite, when β -aminopyridine is formed. The mucate of this base is next prepared and submitted to dry distillation. After a series of complicated reactions, a substance is obtained identical with inactive nicotine. In order to convert this inactive substance into the two optically active modifications, right-handed tartaric acid is employed.

MISCELLANEOUS.

Royal Institution.—At the General Monthly Meeting of the Members of the Royal Institution, held on Monday, the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair, the Chairman announced the decease, on the 30th of November, of Sir Frederick Bramwell, Bart., and the following letter from His Grace the President was read :—

"Alnwick Castle, 2nd December, 1903.

"MY DEAR SIR WILLIAM CROOKES,—It is with the utmost regret that I find an important engagement in Newcastle will unavoidably prevent my attending the Monthly Meeting of the Managers of the Royal Institution next Monday, and the subsequent General Meeting of Members. I am especially grieved because it would have been a melancholy satisfaction to have had the opportunity of expressing my deep sense of the loss the Institution has sustained in the death of our respected and valued friend, Sir Frederick Bramwell. His great talents and high professional reputation are known to all the world—the deep interest he always displayed in the work of the Royal Institution, and the conspicuous services he rendered it, cannot, I think, fail to be within the cognisance of every member. But it is only those who have taken part as his colleagues in the management, and who have had the privilege of enjoying his personal friendship, who can be fully aware of his genial kindness, his wise counsels, and his indefatigable energy. I am glad to think that we were able to do something in his lifetime to convey to him a sense of our esteem when we added his bust to our collection. To us it is a reminder of a loss which will long be felt.—Believe me, Yours very truly,

(Signed) NORTHUMBERLAND."

The following Resolution, passed by the Managers, was unanimously adopted:—

Resolved, That the Managers of the Royal Institution of Great Britain desire to record their deep sense of the loss sustained by the Institution in the decease of Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M.Inst.C.E. His personality, and the signal services he rendered to the Institution by his unvarying devotion to and deep interest in its welfare and in the advancement of experimental research for twenty-seven years as Manager, Honorary Secretary, and Vice-President, will be long remembered. The Managers desire to offer Lady Bramwell and her family the expression of the most sincere sympathy with them in their bereavement.

It was also announced from the Chair that Professor L. C. Miall had been elected Fullerian Professor of Physiology,

Aqueous Solutions of Ammonia.—C. Frenzel.—The author endeavours to solve the question whether in aqueous solution the ammonia is combined with the water in an almost complete manner, forming a very feeble base, or whether the major portion exists simply in solution, a small fraction only being in combination forming a powerful base. The author has already shown (*Zeit. Electrochem.*, vol. vi., p. 477) that the conductivity of liquid NH_3 is considerably diminished by the addition of traces of water, while a subsequent addition exercises only a very feeble influence on the conductivity. The very slight tendency of trivalent nitrogen to change into pentavalent nitrogen, the thermochemical data relating to the history of ammonia, and the hydrolysis of the ammoniacal salts, are all facts in favour of the hypothesis of a feeble base. Ammonia possesses a double function; a very slightly acid one with trivalent nitrogen, and a very strongly basic function with pentavalent nitrogen (NH_4HO , for example); between these two functions a well-defined equilibrium should be established in each case. For the same solution the product of the acid function and of the basic function of the ammonia remains constant, and is independent of the nature of the acid added. The formation of nitrogen in the electrolysis of solutions of ammonia is the result of a secondary action of the anodic oxygen on the solution, $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$. Even concentrated solutions only give small quantities of oxygen.—*Zeit. Anorg. Ch.*, vol. xxxii., p. 319.

MEETINGS FOR THE WEEK.

TUESDAY, 29th. } Royal Institution, 3. (Christmas Lectures
THURSDAY, 31st. } adapted to a Juvenile Auditory). "On Ex-
SATURDAY, Jan 2nd. } tinct Animals," by Prof. Ray Lankester,
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Further particulars on application to the Director—

ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

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Syllabus on application to—

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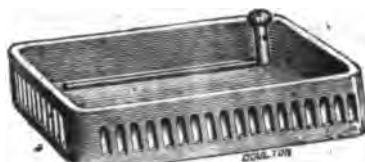
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